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Geoffrey B. Gretton

USE OF AN INCORPORATED HARDENING DEVELOPER TO PRODUCE A PHASE MODULATED HOLOGRAM IN A SILVER HALIDE MATERIAL

by

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A thesis submitted in partial fulfillment
of the requirements for the degree of
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M. S. DEGREE THESIS

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for the thesis requirement for the
Master of Science degree

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A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the Center for Imaging Science in the College of Graphic Arts and Photography of the Rochester Institute of Technology

ABSTRACT

A holographic material is investigated which uses an incorporated hardening developer in a fine grain silver halide emulsion to first obtain a hardening modulation in the gelatin, and then convert the hardening modulation to a refractive index modulation by alcohol dehydration similar to the dichromated gel process. The hardening modulation is observed but conversion to a refractive index modulation by alcohol dehydration is not seen. The feasibility and problems of the material are evaluated.

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1. OVERVIEW OF HOLOGRAPHY

1.1 INTRODUCTION

The original concept of holography was discovered by Gabor in 1947 (1). The discovery did not generate any important practical applications, however, primarily because of the absence of an intense source of coherent light. This problem was solved with the invention of the laser in 1960. Leith and Upatnieks applied the laser to recording holographic imagery in the early 60's and obtained three dimensional imagery which astonished the scientific and lay community(26), and touched off a flurry of predictions of its significance(2-19). Research efforts of the 60's, however, were frustrated by difficulties with the technology, and much of the initial research support dried up by the late 60's. Since the mid 70's, however, there has been a steady regrowth of interest in holography and its application to a variety of technical problems(20-22). A brief mention of some of the main areas of interest follow.

1.2 USES OF HOLOGRAPHY(106)

-Digital data storage

Holographic data storage may be able to provide the high volume, fast access, data storage which is demanded by the

advancing computing technology. The capability of holographic materials for the storage of large volumes of information, and the potential for a non-mechanical read/write capability, offer advantages in this application.

-Two dimensional projection of imagery

A holographically produced image can be projected with an effect much like the projection of a photographic slide. Color imagery is potentially feasible. Advantages include increased brightness, greater durability, reduced cost of duplicated imagery, and a simplified mechanism for a series of projections (moving picture).

-Three dimensional display

Uses of display holography include point-of-purchase advertising and trade show displays, artistic creations using one or a combination of the several effects possible with different recording geometries and materials, security uses such as embossing on credit cards, and documentation of dimensional characteristics of archival materials. Improvements in technology in the areas of duplication of holograms by embossing, the creation of 3D imagery using a series of 2D images with changing perspective, and the

production of color holograms, have made holography increasingly commercially attractive.

-Holographic interferometry

Holographic recording of interference patterns can be applied to all of the classical uses of interferometry, with the holographic plate replacing the recombination beam splitter of a conventional configuration. Holography, however, provides the added versatility of being able to compare any arbitrary wave fronts, including diffuse fronts. Conventional interferometry is limited to nearly planar or spherical wave fronts. Also, holography enables the recording of multiple wave fronts on a single hologram which, when played back, interfere as if they were independent. Because the wave front is recorded, and not observed in real time as in conventional interferometry, stability of a holographic interferometer is limited only to the period of exposure. These advantages have been particularly useful in vibration studies. Extremely accurate contouring of small objects is another useful application of holographic interferometry.

-Pattern (and character) recognition

Pattern recognition systems correlate an input signal with

a known reference signal to determine if the input signal is the same as the reference. Most commonly, this correlation is done by a multiplication of the Fourier transforms of the input and reference signals. Holographic recording provides a convenient means to store the transform plane wave front of the reference signal.

-Image Processing

Other more sophisticated optical image processing methods have been demonstrated using coherent optics. These involve different methods of spatial filtering in the Fourier plane using a holographically recorded spatial filter. Such techniques are also accomplished by computation, but optical processing offers great advantages in the volume and speed of information which can be processed.

-Microscopy

Gabor's original intention when he described holography was to obtain magnification by recording a hologram with an electron beam (very short wavelength), and playing it back with visible light (much longer wavelength). This would result in a large magnification, and a distortion free image if the radius of curvature of the recording beam was

scaled properly by the ratio of the wavelengths of the recording and playback beams. This process turns out to be technically very difficult to do, and present applications of holographic microscopy generally use no wavelength scaling.

The advantage of holographic microscopy is the depth of field which can be imaged. High magnification microscopes can record only a very limited depth of field. If a volume space is to be examined, a holographic image of the space is recorded and then an optical microscope is employed to examine any part of the 3D real image produced by the reconstruction of the hologram. A low premagnification of the space can be employed to relieve, somewhat, the resolution requirements of the holographic recording material. Particle size measurements have been a successful application of this technique. If a pulsed laser is used to produce a series of images, particle flow measurements are possible.

-Holographic optical elements (HOE)

Over the last five years the literature has been flooded with applications of HOEs. The HOE has many of the problems associated with conventional optics, including

aberrations, plus some special problems of its own, including efficiency and dispersion. It is not true that a conventional optical system can be duplicated onto a holographic element with equivalent results. The advantages of HOEs are their ability to provide unusual geometrical configurations or special spectral characteristics. Unusual shapes, low weight, and high spectral reflectivity are examples of useful HOE characteristics. Dichromated gel or photoresist are currently the only recording materials which provide the high efficiency, low noise characteristics needed for HOEs.

1.3 BASIC DESCRIPTION OF HOLOGRAPHY(24)

Holography is a means of recording all the information associated with a given wave front in such a way that the wave front can be accurately reproduced. This is accomplished by interfering the target (source or object) wavefront with a second reference wavefront, and recording the resulting interference pattern with a photosensitive material.

To be recorded successfully, it is necessary that the interference pattern have as great a modulation as possible and be stable over time. The modulation requirement is

fulfilled by using coherent radiation for both the source and reference wavefronts. The laser is the only suitable intense, coherent light source available. Over the surface of the hologram there will be a range of optical path difference. The coherence length of the laser must be sufficient to provide a reasonable intensity modulation in the interference pattern for this range of optical path difference. The stability requirement is fulfilled by recording in an environment carefully isolated from any vibration. Figure 1.2-1 illustrates a sample configuration for recording a hologram.

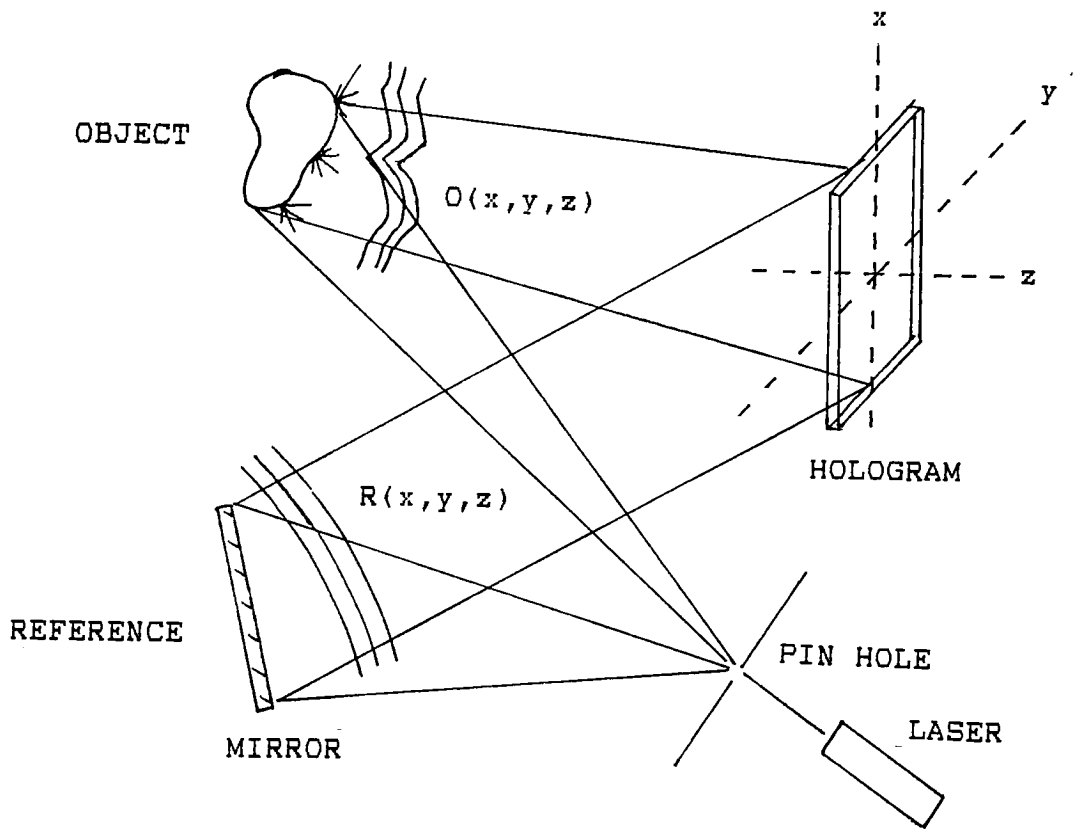


Figure 1.2-1 Sample configuration for recording a hologram.

In Figure 1.2-1, O(x,y,z), the object beam, is the wave front resulting from the reflection of the illumination from the laser from a diffuse object, and R(x,y,z), the reference beam, is a spherical wave front. This particular combination of wave fronts is not significant, however, and

O and R can be considered completely general. If a photosensitive material is at plane z, and the polarizations of O and R are parallel, an interference pattern results. The wave fronts O and R can be written(23)

$$O(x,y) = \vec{o}(x,y) \cos[2\pi\nu t + \phi_{o(x,y)}]$$

$$R(x,y) = \vec{r}(x,y) \cos[2\pi\nu t + \phi_{r(x,y)}]$$

where $\vec{o}(x,y)$ and $\vec{r}(x,y)$ are vector amplitudes of the object and reference waves and ϕ_o and ϕ_r are the phases of the object and reference waves. Although the amplitudes are vector quantities, if we assume that they are parallel polarized, they can be treated as scalars.

The intensity I(x,y) of the interference pattern formed on the hologram can be represented by(23):

$$I(x,y) = o^2(x,y) + r^2(x,y) + 2\, o(x,y)\, r(x,y) \cos[2\pi(\xi_o - \xi_r)x + \phi_o(x,y) - \phi_r(x,y)]$$

Where: $o(x,y)$ and $r(x,y)$ are the amplitudes of the object and reference waves.

$\phi_{o(x,y)}$ and $\phi_{r(x,y)}$ are the phase of the object and reference waves.

$$\xi_o = (\sin\theta o)/\lambda$$

$$r = (\sin\theta r)/\lambda$$

λ = wavelength, and θ is the angle at which the wave

propagates with respect to the normal to the hologram. The term $2\pi(\xi_o - \xi_r)x$ accounts for phase variation resulting from path differences to any given point on the hologram.

It can be seen that the intensity pattern on the hologram depends on the amplitude and the phase of the object and reference waves. The maximum intensity available anywhere in the interference pattern is dependent on the amplitude interaction, and the spatial distribution of the intensity is dependent on the phase interaction.

The holographic recording material records the intensity variations of the interference pattern. These intensity variations can be recorded in the form of transmittance variations in the material, and holograms recorded in this manner are referred to as amplitude modulated holograms. The intensity variations can also be recorded as phase modulation in the recording material by variation of the refractive index, the thickness of the material, or by variations of the surface profile of the material. Such holograms are called phase modulated holograms.

If the interference pattern is recorded with a material which is thin in comparison to the spatial intensity

distribution of the interference pattern, the hologram is referred to as a plane hologram. If the thickness of the material is large in comparison to the spatial intensity distribution, a volume hologram results. In this case, a three dimensional recording of the aerial interference pattern is recorded within the volume of the recording material.

To play back the hologram without abberation, the developed hologram is illuminated with the original reference wave front. In the case of a thin amplitude hologram, the amplitude of the reference (play back) wave front is modulated by the hologram. The amplitude modulation introduced by the hologram results in three different wave fronts propagating in three different directions. One of these wave fronts is proportional to the original object wave front.

In the case of a thin, phase modulated hologram, the phase of the reference (play back) wave front is modulated according to the intensity distribution of the interference pattern recorded on the hologram I(x,y). Thus, the wave front resulting from the playback of the hologram is:

$$W(x,y) = r(x,y) \cos[2\pi\nu t + \phi_r(x,y) + \phi_h(x,y)]$$

where

$$\phi_h(x,y) = p\ I(x,y)$$

The factor p is an index of phase modulation. This interaction between the reference wave and the hologram results in many wave fronts, one of which is proportional to the original object wave front. If p is small, the wave front which duplicates the original object wave front is the most intense, and can be reconstructed with a minimum of noise. The requirements for linear amplitude and phase recording are discussed in Section 2.1.2.

Photographic emulsions are capable of recording the intensity distribution of the interference pattern as both amplitude and phase variations in the emulsion. This effect has not been extensively studied(23).

To record a successful hologram, the spatial distribution of the interference pattern of the object and reference wave fronts must be within the resolution constraints of the recording material. Consider Figure 1.2-2(24).

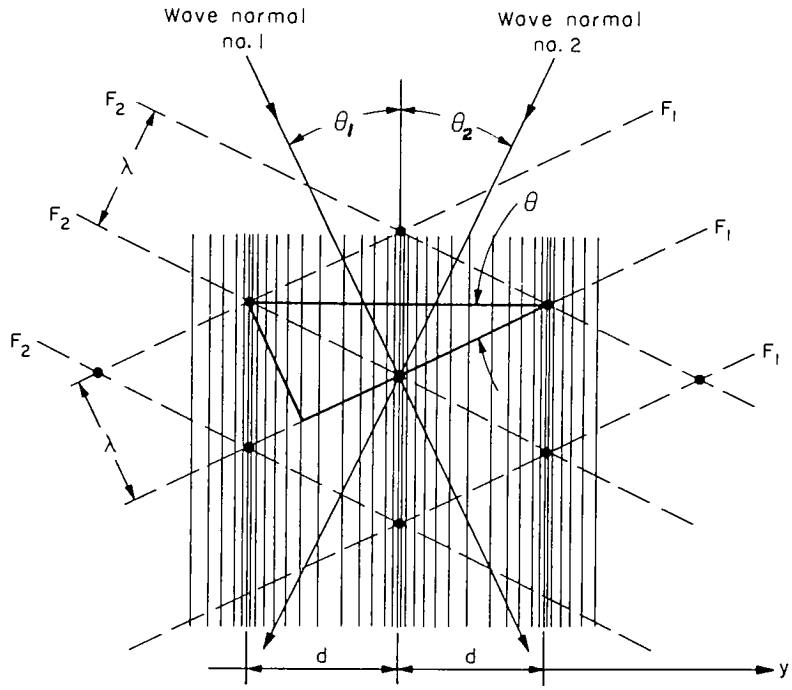


Figure 1.2-2 Interference pattern of two intersecting plane waves.

The object and reference waves are plane waves of wavelength λ impinging on the hologram at angle Θ from the normal to the hologram. The distance d between the fringes of the resulting interference pattern can be seen, from the heavy lined triangle, to be related to Θ and λ by the equation:

$$2d \sin\Theta = \lambda$$

This analysis is general for any wave front since any front can be broken into the sum of many plane waves. For the interference of waves which strike the plane of the hologram at non-equal angles from the normal, the expression becomes

$$d\,(\sin\Theta_1 - \sin\theta_2) = \lambda$$

where the angles on opposite sides of the normal are of opposite sign(25).

The spatial frequency of the interference pattern (1/d) must fall within the resolution capacity of the recording material, or the fringe pattern will not be recorded. As the difference in angle between the object and reference beam increases, so the spatial frequency of the interference pattern increases, and the demands on the recording material increase. Thus, the size of a hologram is often limited by the resolution of the material. The spatial frequency range of a hologram is often called the band pass of the hologram.

The geometry of the optical setup for recording a hologram dictates the type and characteristics of the resulting hologram. In Figure 1.2-3, representative exposure geometries are illustrated(24).

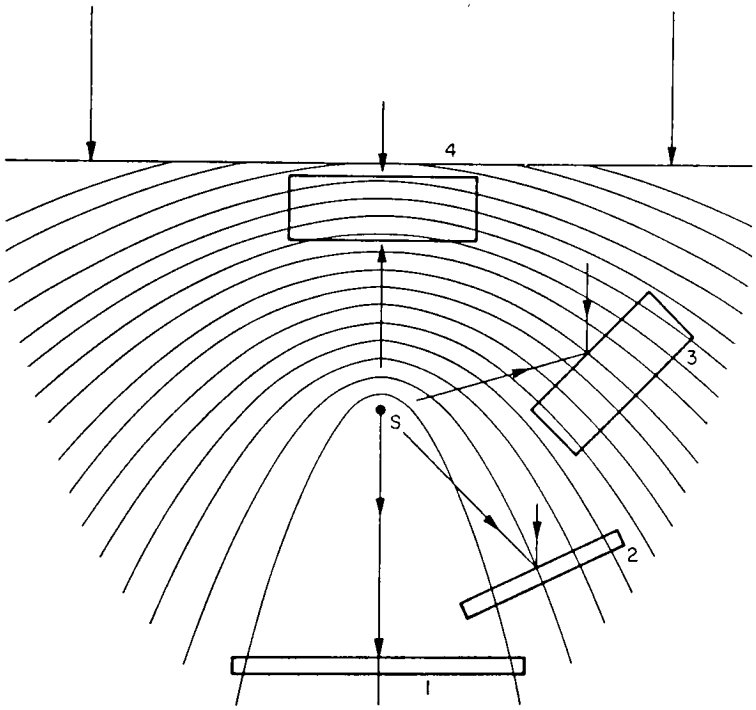


Figure 1.2-3 Representative exposure geometries. Contours represent locations of maximum intensity of the interference pattern resulting from the interference of a point source at S and a plane wave from the top of the figure.

Position 1, an "in line" or "Gabor" configuration,

represents the position of lowest spatial frequency range of the interference fringes. Gabor(1) used this configuration in his original work in 1948 because it is the most forgiving in terms of the requirements for coherence of the light source, and the resolution of the recording material. Because of the wide fringe spacing relative to the thickness of the recording material, it is a plane hologram. Playback of the hologram is by transmission of light through the hologram, and is therefore termed a transmission hologram.

Position 2, an "off axis" configuration, was introduced by Leith and Upatnieks in 1962(26). This configuration was made possible by the introduction of the laser with its high coherence. It is still considered a plane hologram since the fringe spacing is, again, large relative to most recording material thicknesses. The primary advantage of this configuration is that, on reconstruction, the diffraction order containing the object wave front is separated from the other two diffraction orders produced by

an amplitude hologram. In the "in line" configuration these orders overlap and contribute a great deal of noise to the desired object wave front.

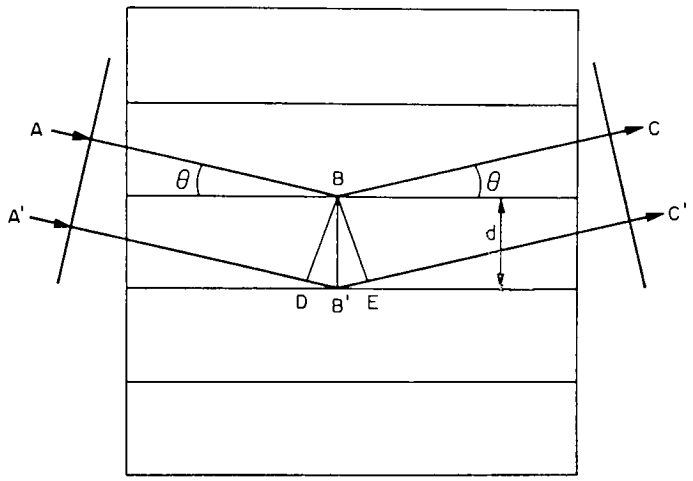


Figure 1.2-4 Volume diffraction grating.

$DB' + B'E = 2d \sin \Theta = \lambda$

Position 3 in Figure 1.2-3 produces a "Bragg-effect" hologram. With an angle between the object and reference waves approaching 90^{o}, the fringe spacing is small relative to the recording material thickness, and a volume hologram results(27). The average dielectric constant, the amplitude and spacing of the fringe pattern, replay wavelength, and grating vector are all factors which influence the size of the fringe spacing(28). In this configuration, the interference fringes can be thought of

as planes of intensity within the recording material. For a photographic emulsion, development converts these planes of intensity to planes of density by intensity-wise deposition of elemental silver. If these planes are thought of as partially reflecting surfaces, they can be treated according to Bragg's law.

Figure 1.2-4(24) illustrates the configuration of partially reflecting planes within an emulsion, and a trigonometric analysis results in the familiar Bragg equation

$$2d \sin \Theta = \lambda$$

The Bragg equation indicates that, for a given fringe spacing d, a given wavelength will interfere constructively only at one angle. This leads to the interesting possibility of an "amplitude" recording material being able to act as both an amplitude modulator and a phase modulator of the reference (play back) wave front. The amplitude modulation of the reference front results from the varying reflectance of the internally recorded fringes. The reflectance is proportional to the amplitude of the interference fringe, and is the encoded amplitude information of the original object wave. The phase modulation of the reference (play back) wave results from interference effects within the emulsion, controlled by the

relative spacing of the internally recorded fringes. The fringe spacing is, therefore, an encoded record of the phase information of the original object wave front.

Another important characteristic of a volume hologram is the supression, upon reconstruction, of diffraction orders other than that diffraction order carrying a wave proportional to the original object wave(24). This results in a much larger amount of the incident reference wave being directed into the desired reconstructed object wave front, and a much more efficient hologram. The supressed diffraction order is, in fact, not lost and can be reconstructed by illuminating the hologram from behind with the exact same reference wave, but traveling now in exactly the opposite direction.

If the fringes within the volume of the emulsion result in phase modulation of the recording material, for example variations in refractive index, a similar result is obtained with the added advantage of, theoretically, 100% efficiency in directing the reference wave into a reconstruction of the original object wave. The visualization of the interference effect is, however, difficult, and the mathematics, happily, far beyond the

scope of this introduction. The development of the theoretical explanation of these interference effects is still in progress, and uses coupled wave theory. Syms and Solymar(28) is a good reference for an overview of work on coupled wave theory.

Position 4 in Figure 1.2-3 results in a "reflection" hologram. This configuration was introduced by Denisyuk in 1962(29). It is a volume hologram, with fringe spacing approaching $\lambda/2$. This is, by far, the most demanding configuration in terms of the required recording material resolution. Also, note should be taken that the fringe pattern is nearly parallel to the surface of the emulsion. This results in a reversal of direction of the reference wave and, thus, the name reflection hologram. The wave reflected back is proportional to the original object wave and is, again, the result of complex interference phenomena within the recording material.

The reflection hologram is extremely angle and wavelength specific; so much so, that the hologram can be viewed with white light. At the proper angle, the wave reflected back has such a narrow frequency band width, that there is no visible chromatic aberration (multiple images of various

colors). Again, the fringes can be phase modulations, in which case the effect can be likened to a very complex lens antitransmission coating.

2. OVERVIEW OF RELEVANT HOLOGRAPHIC RECORDING MATERIALS

2.1 INTRODUCTION

The ideal holographic recording material must possess a number of important characteristics. First, to achieve maximum efficiency, it must be a phase material and capable of recording a volume hologram. To record a volume hologram, the ideal material must be relatively transparent during exposure.

The material must possess extremely high resolution capability, preferably on the molecular level. This would provide maximum band pass for a given holographic recording. Also, the absence of a particle structure would eliminate the serious degradation introduced by scatter of any kind, both at the time of recording and during playback.

The ideal recording material must be as sensitive as possible at the wavelength of the laser intended to be used. Higher sensitivity permits shorter exposure times, easing the problem of holding the object still during exposure (less than a quarter wavelength of movement or, preferably, none at all). Also, larger formats become possible at a given laser power.

Lasers which are most suitable for holography, because of their coherence length and power available, are the helium neon, the argon and the krypton. The helium cadmium laser is a relatively inexpensive laser which lases in the blue (441.6 nm) but suffers from a relatively short coherence length. Presently, the helium neon laser at 633 nm. is the least costly and most common laser available, but is a low power laser. The argon emits a number of wavelengths from IR to UV, and is capable of high power, but is very expensive due to inefficiency (power requirements and need for water cooling). Dependable air cooled argons have recently become available but are still relatively expensive. The krypton is similar to the argon except it operates in the red and IR portion of the spectrum.

There are, however, lasers under development which will perhaps provide useful coherent radiation over the spectrum mentioned above. Examples are the recent development of mode locked diode lasers which lase in the IR and red, continuing work on X ray lasers, and green, yellow and IR lasing helium neon lasers. Presently the cheapest sources of laser power are in the red and IR and spectral sensitivity of an ideal recording material in this wavelength region would be

a good place to start.

2.1.1 USEFUL HOLOGRAPHIC RECORDING MATERIALS

The choice of a specific recording material is dependent on the particular application. Following is an indication of the presently most useful materials and their applications(30).

Photoresist records the diffraction pattern in the form of a surface relief after development. It is particularly useful, in that the relief pattern can be duplicated using thermoplastics. Sensitivity is relatively low, and spectral response is in the blue region only. Applications have been in the production of diffraction gratings and display holograms and trinkets.

The demonstration by Kramer(31) that deep groove gratings in photoresist with high aspect ratios can result in very high diffraction efficiency, has made photoresist a potentially useful material for holographic lens elements. Gratings of this type are, however, relatively difficult to produce and are too fine to replicate with thermoplastics.

Photopolymers can be used to record a volume hologram of

refractive index (RI) modulation with resolution at the molecular level. The RI modulation is the result of polymerization initiated by light. Spectral sensitivity can be controlled by the addition of sensitizing dyes. Low sensitivity and short shelf life have been the main problems with photopolymers. Applications have been in real time interferometry and rapid hologram copying. Potential applications are in display holography and HOEs.

Thermal recording materials employ local deformation or phase change of the recording material due to heat to record a hologram. Most work has been done with pulsed lasers, but continuous wave lasers have been used. Advantages include speed of recording and low cost of materials. Disadvantages include low resolution and limitation to plane hologram recording. The main application is in interferometry.

Photothermoplastics use a multilayer structure of a photoconductor, a thermoplastic and a conductive layer. Exposure causes an intensity-wise modulation of voltage. Upon mild heating, the thermoplastic is deformed by the potential difference and results in a thin phase hologram. Stronger heating erases the hologram and makes the material

ready for reuse. Diffraction efficiencies of up to 35 percent and resolution of 2000 lines/mm can be obtained. Problems include "frost", a random surface modulation of unexplained origin, and "memory" effects after erasure. Rapid, in situ development, and the possibility of erasure and reuse, coupled with relatively high pan-chromatic sensitivity and diffraction efficiency, make photothermoplastic materials very attractive for applications such as hologram interferometry, holographic memories and optical information processing.

Photochromic materials undergo molecular level, reversible changes in color when exposed to light. Organic materials have been studied but are prone to fatigue and a limited life. Inorganic doped crystals have been more successful in terms of lifetime and ability to perform write, read, and erase operations, but are low in sensitivity. The primary application is in information storage.

Photorefractive crystals display a volume molecular level refractive index change caused by intensity wise rearrangement of electrons within the crystal. Characteristics depend on the crystal system, but high resolution, high sensitivity, high efficiency, and

unlimited recyclability have been obtained (not necessarily all at the same time). A major problem is the readout beam degrading the stored image. Such crystals also are highly optically active, and some advantage has been taken of the difference in polarization of the diffracted beam and the scattered light. Applications include optical computing, image filtering, and information storage.

Fine grain silver halide materials have been the most commonly used holographic recording materials. Reasons for this include high sensitivity and a wide range of spectral response, high resolution capabilities, capability of recording plane, volume, phase and amplitude holograms, low cost and availability, good shelf life, and stability after processing. Processing, although straight-forward, is multistep and wet. The presence of a grain structure which introduces scatter is also a disadvantage. Silver halide materials are discussed further in Section 2.3.

Dichromated gelatin produces a phase modulated (by refractive index change) volume hologram, which is characteristically highly efficient. Resolution is on the molecular level and scatter is minimal. It would, in fact, be a very ideal holographic recording material if it were

not so difficult to obtain reproducible results. The mechanism of formation of dichromate is complicated, it lacks shelf life, and results are influenced by a multitude of experimental parameters. In addition, it is insensitive, and its spectral response is in the UV and blue, necessitating the use of an expensive argon laser. Dichromated gel is discussed further in Section 2.2.

Other material(35) which have received attention in the literature are electro-optical devices, dry silver, amorphous semiconductors, vesicular films, diazo films, and free radical films.

2.1.2 Characterization of Holographic Recording Materials

A holographic recording material can be characterized in terms of three variables(32), the fringe visibility (V), exposure (H), and diffraction efficiency (n). Fringe visibility is defined as(107):

$$V = I_{max} - I_{min} / I_{max} + I_{min}$$

where I_{max} and I_{min} are the maximum and minimum intensities of the interference fringes. If two waves interfere, the fringe visibility depends on the amplitudes of the two waves, the temporal coherence of the waves, and the angle

between the direction of polarization of the waves. If the following quantities are defined:

$|U_T(t)|$ = complex degree of temporal coherence

Θ = angle between the direction of polarization of the waves

R = intensity ratio of the waves = $(r/s)^2$ where s and r are the amplitudes of the subject and reference waves respectively

then the fringe visibility is described as(33)

$$V = 2\,|UT(t)|\,\sqrt{R}\,\cos\Theta\ /\ (R + 1).$$

If the path difference between the beams is small compared to the coherence length of the laser, the degree of temporal coherence can be considered one. If the polarization of both waves is perpendicular to the plane of incidence, the angle between the polarizations will be 0° for all angles of incidence of the two waves, and the cosine will always be one. These condition are best met by using two plane waves with the optical path difference between the two beams kept to a minimum, and the polarization of both waves kept carefully perpendicular to the plane of incidence. Under these conditions, the fringe visibility becomes:

$$V = 2\sqrt{R}\ /\ (R + 1)$$

Say a thin material is given an exposure, H(x), from two interfering beams over a small area A:

$$H(X) = H_o + H_1(X)$$

where

$$H_o = [r^2 + s^2]\, T \qquad T = \text{time}$$

and $H_1(X)$ designates the modulation of intensity by the interference of the waves with each other.

The intensity of the reconstructed wave is related to the fringe visibility by:

$$Iv = 1/4\, [v\ t(H_o)\ H_o\ V]^2$$

where v is the amplitude of the reconstructing wave (would be the same as r), and $t(H_o)$ is the complex transmittance of the material.

For the hologram to be "linear", the complex amplitude of the reconstructed wave must be proportional to that of the subject wave over the whole hologram. For this to be true, the complex transmittance of the hologram must behave as follows:

$$dt/dH = \text{constant}$$

For linear recording, the complex amplitude transmittance of the material must respond linearly to exposure over the

exposure range

$$H_{min} < H < H_{max}$$

where the range of H is determined by the interference term of the interaction of the subject and reference waves. In terms of the fringe visibility, the range of exposure takes the form

$$H_o (1 - V_{max}) < H < H_o (1 + V_{max}).$$

If the complex transmittance of a recording material is designated(108)

$$t = t \exp (i \phi)$$

then

$$dt/dH = dt/dH \exp(i \phi) + it \exp(i \phi) \, d\phi / dH.$$

Whether the material is an amplitude or phase material depends on which value, dt/dH or $d\phi/dH$, is the larger finite value. It is possible, for example with silver halide materials, that both amplitude and phase components of the complex transmittance are modulated.

For an absorption material, the condition for linear recording is

$$dt/dH = \text{constant}$$

and the range of exposure must lie on the linear portion of

the amplitude transmittance vs exposure curve of the material.

For a phase material, the condition for linear recording is

$$\exp(i\phi)\, d\phi(H) / dH = \text{constant}$$

However, this equation only has the trivial solutions ϕ = constant and $d\phi/dH = 0$. Thus, strictly speaking, it is not possible to achieve linear recording with a phase material. For a small but finite $\phi(H)$, $\exp(i\phi) \cong 1$, and the condition for linearity becomes

$$d\phi(H)/dH = \text{constant} \qquad \phi(H) \ll 1$$

In practice, although the phase shift vs exposure is only linear for small values of exposure, the non-linearity introduced by larger exposures is tolerable.

If the fringe visibility is made to be 1, that is the beam ratio (R) is equal to 1, the minimum value of exposure Ho(1-Vmax) will be zero. Since many recording materials, including silver halide materials, are not linear in amplitude transmittance down to an exposure of zero, it is necessary to keep the fringe visibility less than unity over the whole hologram(32). This is accomplished by

keeping the beam ratio greater than 1 over the whole hologram. Keeping R > 1 ensures that the bias exposure needed to bring the material within the linear response range of amplitude transmittance comes from the reference beam. This is a much more practical situation than attempting to ensure that the entire object beam is sufficiently greater in intensity than the reference beam over the entire hologram in order to obtain a fringe visibility everywhere less than one.

For a perfect recording material, the reconstructed wave front of a hologram is perfectly proportional to the subject wave. As developed by Collier(34) the perfect reconstructed wave complex amplitude from a hologram exposed by the interference of two plane waves is

$$W_o(x) = w_o \exp[i(2\pi\xi_s x + \delta)]$$

where $w_o = S\ r\ H_o\ V$

and ξ_s = the spatial frequency of the subject wave.

S is a complex constant referred to as the holographic sensitivity. If S is a constant independent of the average exposure H_o, the fringe visibility V and the spatial frequency of the signal wave ξ_s, over the entire hologram, the recording is perfectly linear.

The diffraction efficiency n is defined as

$$n = w_o^2 / r^2$$

and can be written as

$$n = S H_o V .$$

If the average exposure is constant over the hologram, which is nearly true for the case of two plane waves, then n vs. V with H_o the parameter can be plotted. For a perfect material, the plots would be linear as in Figure 2.1.2-1(34).

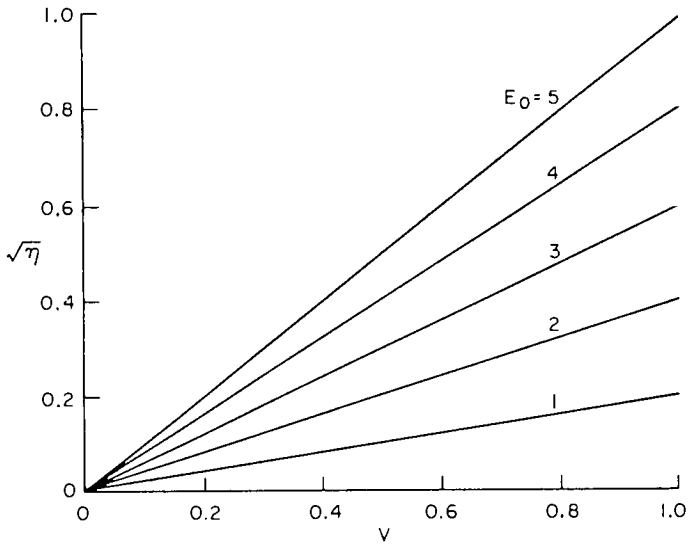


Figure 2.1.2-1 n vs. V characteristics for an ideal recording material. n is diffraction efficiency, V fringe visibility, and Eo is average exposure (arbitrary units).

For real materials, S is not an independent constant over the hologram. Factors which can contribute to the imperfect behavior of a recording material are:

1. Random scatter of the subject and reference beams during exposure by the recording material.
2. Random scatter of the reconstructed beam by the processed recording material.
3. Spatial modulations of the reference and reconstruction waves.

4. Nonlinear recording of the signal wave.
5. Inhomogeneities and surface deformations of the recording material.

An example of the n vs. V (H_o the parameter) plot for a real material at a given angle between the subject and reference wave is given in Figure 2.1.2-2(34).

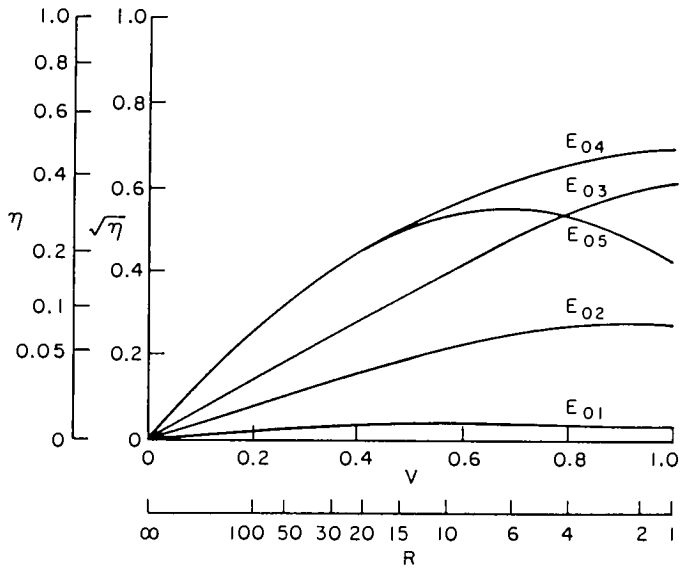


Figure 2.1.2-2 n vs. V characteristics representative of a real recording material. R is the beam ratio (ref./object).

This characterization of a real material is valid for any type of hologram and any recording material. Information which is readily extracted from this plot is:

1. Range of fringe visibility (or beam ratio) for which the hologram recording is linear.
2. Maximum achievable diffraction efficiency.
3. Exposure necessary to obtain a given diffraction efficiency.
4. Optimum value of average exposure, representing the best compromise between linearity and efficiency.

2.1.3 Evaluation of Holographic Recording Materials

The evaluation criteria of holographic recording materials are, at present, very ill defined. Often the term "lines per mm" is used to indicate the resolution of a recording material. This term indicates the maximum capability of the material to resolve spatial variations of an interference pattern. The term is a carry-over from the visual evaluation of photographic materials, and indicates the maximum frequency which is visually recognizable in a photograph by the human eye (with magnification). When used in terms of holographic recording materials, it is next to meaningless because it gives no indication of the modulation which is achieved within the material at the specified frequency and is, for most high resolution recording materials used in holography, beyond the measuring capability of existing instrumentation.

The modulation transfer function would be a much better indication of a material's recording capability. However, measurement of modulation at the frequencies employed in holography is beyond the capability of existing instrumentation.

A indirect measurement of the MTF of a material by measuring the performance of the material under specified conditions is difficult because of the large number of factors introduced in exposing and processing a hologram. Such factors as average dielectric constant, deformation of the material, phase or amplitude modulation, the degree of modulation falloff with depth into the material, hardening effect, grain size influences on refractive index and scatter, and existence of spurious gratings as well as the degree of modulation all effect performance. This, plus the fact that present theoretical explanations of the interference effects within a hologram are incomplete makes it impossible derive modulation based on performance of the material.

For silver halide materials, the specification of grain size distribution has been a somewhat useful indication of the capability of a given material.

Investigators of holographic materials generally choose a simple recording geometry which ensures the recording of a thick or plane hologram, as desired, and simple object and reference wave fronts, usually plane waves. A comparative study can then be conducted using the diffraction efficiency of the resulting hologram as the evaluation criteria. If the hologram is recorded in such a way that the fringe pattern is not perpendicular to the surface of the hologram, the recording material distortions can be determined by measuring changes in the Bragg angle. Efficiency can be measured by measuring the energy deflected into the diffraction order of interest or by measuring depletion of the zeroth order. Scatter and absorption are usually measured by calculating the energy difference between the reconstruction wave and the sum of all the diffraction orders.

The diffraction efficiency can be an absolute or a corrected measurement. An absolute measure would be the actual energy ratio between the reconstructed wave and the reference wave. A corrected measurement would take into account the enery lost by reflection at each interface in the reconstruction configuration (for example the glass air interface for a photographic plate). A corrected

measurement would, of course, lead to a higher calculated efficiency of the hologram than the absolute measurement. Such correction for reflections are either calculated using Fresnel's equations, taking into account the polarization, or estimated.

The reflections mentioned in regard to playback efficiency of the hologram are also of concern during exposure(99). All wave fronts present during exposure will be recorded as part of the hologram, including wave fronts resulting from any reflections or scattering of either the object or reference wave fronts. The result of the recording of reflections or scatter in the original hologram is, upon playback, reduced signal to noise ratio and efficiency. The recordings resulting from reflections are often called spurious gratings. Reflections are generally minimized during recording and playback by using index matching tanks and antihalation backings.

Scatter is a problem with any recording material where scattering centers are present. Scattering problems are best solved with extremely fine grain recording materials or, preferably, with no grain at all, such as with dichromated gel.

The speed of holographic recording material is usually indicated in ergs per cm^2 or joules per cm^2 and indicates, usually, the exposure necessary to obtain a density of 1.0. For a phase recording material, such as dichromated gel, where density is not obtained, there is no accepted criterion for exposure in measuring sensitivity.

2.2 DICHROMATED GELATIN (DCG)

2.2.1 Introduction

Dichromated gel is used where highly efficient, low noise holograms are essential. The making of holographic lens elements and display applications have been the main uses of DCG.

The advantages of DCG stem from the fact that DCG is a clear, grainless organic polymer (gelatin) which records intensity variations in the form of refractive index variations within the gelatin. Being grainless, scatter is kept to a minimum and the transparency of the emulsion minimizes absorption of radiation and maximizes efficiency. The phase modulation is on the molecular level so recording material resolution is extremely high.

Some desirable properties of dichromated gelatin are summarized in Table 2.2.1-1(38).

PROPERTY	TRANSMISSION	REFLECTION
Achievable Diffraction Efficiency(DE)	>95%	>95%
Practical Thickness	<100 micron	<100 micron
Minimum Thickness for High DE	5 micron	5 micron
Thickness Control by Processing	±20%	±20%

Table 2.2.1-1 Properties of dichromated gelatin.

The problems with DCG are in sensitivity and reproducibility. Dichromate absorbs from 250 nm. to 520 nm. and is most sensitive at 360 nm. The spectral sensitivity of dichromate can, however, be extended into the red by addition of suitable sensitizing dyes such as methylene blue and methylene green(37,38). An idea of the exposure requirements for DCG can be gained from Table 2.2.1-2(38). Reproducibility is a problem because of the large number of physical parameters which influence the process.

MATERIAL	SENSITIZER	SPECTRAL SENSITIVITY (nm)	EXPOSURE REQUIRED* (mj/cm^2)	ACHIEVABLE RI MODULATION
Dichromated Gel	$(NH_4)_2Cr_2O_7$	250-520	50-100 at 514.5 nm	0.08
Dye-Sensitized DCG	$(NH_4)_2Cr_2O_7$ + dye	red	500-1000 at 532.8 nm	0.02

*Exposure level which produces a refractive index modulation larger than 0.015.

Table 2.2.1-2 Exposure requirements of dichromated gelatin.

When compared to silver halide materials (.002 to .2 mj/cm^2) the relatively high exposure required is clear. It should be mentioned that the exposures reported in the literature are not very consistent and the above exposures are only an indication.

Chang and Winick(39) have reported the use of silver halide material followed by a hardening bleach (a modified acid dichromate), and subsequent dichromate-like processing to produce dichromated holograms. Such holograms would have a sensitivity equal to the original sensitivity of the silver halide material.

The large exposure required and the spectral sensitivity of DCG necessitates the use of a high power argon laser.

Power requirements also limit the practical size of the hologram to under 80 square inches.

The preparation and processing of a dichromate hologram are outlined below, along with the more important factors which influence the results. This information is extracted from several references(38,39,41-44,98). Reports of experimental findings vary widely, and researchers who have worked extensively in the field have indicated that a complete description of dichromated gel experimental parameters has yet to be published(45) and that strict reproducibility with DCG is virtually impossible(46).

Coating:

The first step is obtaining a gelatin film. This is accomplished by coating the gelatin by an accepted method (doctor blading, dip etc.)(47,98) or by removing the silver halide and dyes from a commercially available silver halide material to obtain a pure gelatin coating(48-50,43). The coating thickness effects sensitivity(51). Coating should be in a clean environment (class 100 filtered booth(44)). Temperature and humidity during drying influence the crystaline state of the gelatin(40). An amorphous state is desired and drying at 25-45°C has been found to be

best(38,63).

Pre-hardening:

The gelatin must be pre-hardened before exposure to prevent the gelatin from dissolving in the processing baths, and to optimize the quality of the hologram. For a user prepared coating, this is sometimes accomplished using the dark reaction of dichromate(42,44). Dichromate is dissolved in the gelatin, and the degree of pre-hardening is influenced by concentration of dichromate, amount of ageing of the coating, humidity, temperature, and the particular gelatin used. Other inorganic and organic hardeners may be used such as chrome alum or formaldehyde(60).

The degree of general hardening is a critical factor in the process. Too little creates a noisy hologram and too much, an inefficient hologram(38,51). General hardening is a factor in thickness control(38). The amount of general hardening can be further controlled during development.

A commercial silver halide plate is already pre-hardened, usually too much and inconsistently from batch to batch. It is usually subjected to a hot water treatment to soften the gelatin (51,52,63).

Sensitization:

After pre-hardening, the gelatin layer is sensitized by soaking in a dichromate solution. It is generally desired to obtain the maximum amount of dichromate in the gelatin without crystalization when the coating dries (up to a 20% solution(51)). The concentration and drying conditions (relative humidity and temperature) are important(38,52). Concentration of sensitizer can be used to control final thickness(38).

Exposure:

Too intense an exposure can cause bowing of the glass from strains caused by the cross-linking of the gelatin(42). Humidity and temperature are critical. Exposure causes a dark stain to be formed in the coating from the production of Cr^{+3} ion. This stain decreases the transmittance of the gelatin layer with increase in exposure. Important variables are sensitizer concentration, delayed development, beam ratio, spatial frequency of the interference pattern, and exposure rate(52).

Water development:

This step involves soaking in water to swell the gelatin and dissolve out the dichromate. The differential in

swelling (caused by the hardening differential created during development) creates a refractive index modulation, and high efficiency can be observed(38). Transfer of gelatin molecules from unhardened to hardened areas may take place(38,51). Increasing temperature can increase the swell differential and improve diffraction efficiency(41). pH is also important(51). No mention is made of how pH is important.

Post hardening:

A hardening bath is sometimes employed after the water development to further increase the bias hardness introduced by the pre-hardening step. A chrome or potassium alum hardening fix bath, hardening wash or a dichromate solution is usually used(38,51).

Alcohol development:

A rapid dehydration of the gelatin is effected by bathing the gelatin in isopropyl alcohol (other water miscible solvents are possible but isopropyl is most often used(51)). The alcohol is sometimes hot (up to boiling)(51,44,52). To produce a narrow spectral banded hologram, the dehydration is done in two steps, the first step being an alcohol-water mix (usually 50/50) and the

second, 100% alcohol. For a broad spectral band hologram, a violent dehydration is effected with a single bath of boiling 100% alcohol(51).

Drying and Preservation:

DCG holograms are dried slowly at room temperature, or rapidly under hot air. The temperature of drying can be used to control thickness(38). Relative humidity must be low.

The final hologram is very susceptible to moisture. Rewetting the gelatin destroys the hologram, but it can be reformed by a second alcohol dehydration. Holograms are sometimes dried by baking (1-2 hrs. at 90°C) or by vacuum dehydration(38) and are always protected by cementing a cover glass over the gelatin coating.

Sample Procedure(52) for DCG Hologram from a Commercial Plate:

Unless noted, all baths are at 68°F.

STEP	TIME
1. Soak in non-hardening fixer.	10 min.
2. Wash at 90°F. Start at 68°F and raise temp. 2.5°F/min. to 90°F. Following wash, lower temp. at same rate to 68°F.	5 min.
3. Soak in standard hardening fixer.	10 min.
4. Wash in running water.	10 min.
5. Rinse in distilled water with agitation.	5 min.
6. Rinse in Photo-Flo 200; 1 drop/500ml. Wipe off excess.	30 sec.
7. Dry overnight in horizontal position at room temp.	
8. Soak in 5% ammonium dichromate solution with 0.5% Photo-Flo. Wipe off excess.	5 min.
9. Dry overnight in horizontal position at room temp.	
[EXPOSE]	
10.* Soak in 0.5% solution of ammonium dichromate.	5 min.
11.* Soak in hardening fixer.	5 min.
12. Wash in running water.	10 min.
13. Rinse with 1 drop/500ml Photo-flo. Wipe off excess.	30 sec.
14. Soak in distilled water with agitation.	2 min.
15. Dehydrate in 50/50 solution of isopropanol in distilled water.	3 min.
16. Dehydrate in 100% isopropanol.	3 min.
17. Dry at room temp.	>½ hr.
18. Dry by baking over a hot plate or in a vacuum chamber.	2 hr.

* post hardening steps

2.2.2 Mechanism of the Dichromated Gelatin Process

Dichromated colloids are one of the oldest known photosensitive materials, yet the mechanism of the photochemical reaction is not well understood(53). It is believed that the Cr^{+6} ion is reduced to Cr^{+3} by radiation, and the Cr^{+3} ion effects a cross-linkage between the carboxylic groups in the gelatin matrix. Most recent work assumes that the chromium ion is incorporated into the cross-link. This cross-linkage results in a differential hardening, and a corresponding differential solubility of the gelatin. Advantage has been made of this differential solubility in the production of printing plates.

The mechanism of formation of dichromated gelatin holograms has received considerable attention in the literature. Shankoff(54), the originator of the method, proposes that the refractive index modulation is the result of the formation of microcracks in the gelatin. He proposes that the microcracks result in a surface relief pattern of fissures in the surface of the gelatin in planar holograms, and an onion skin arrangement of fissures in volume holograms. It is proposed that the microcracks are the result of strains caused by the differential hardening, and sudden dehydration of the gelatin layer. These

observations are backed up by micrographs showing the onion skin effect and experimental data consistent with this theory(55).

Meyerhoffer(56) points out some problems with the microcrack theory, particularly, the ability of DCG to form efficient multiple exposures of different object waves. He also mentions the existence of a chromium desiccant complex of high refractive index which could contribute to the RI differential, but concludes that the difference in RI between the complex and gelatin is not enough to fully account for the RI modulation observed in DCG holograms. The structure of the complex is not mentioned, or adequately referenced.

Lin(48) proposes a volume RI modulation, but shows no experimental evidence.

Case and Alferness(57) propose the existence of voids on the molecular level resulting in an effective dielectric modulation (which amounts to a volume RI modulation). They successfully modelled the RI modulation vs. exposure of dichromated holograms based on the modulation of dielectric constant and differential absorption of the gelatin with

exposure. The differential absorption with exposure is caused by the formation of the brown Cr^{+3} ion when the hologram is exposed.

Chang(38) maintains that the crack theory does not explain why:

a. The diffraction efficiency of a properly developed hologram does not change in either xylene or isopropanol.
b. A hologram processed properly has extremely low scattering noise.
c. Diffraction efficiency of an erased hologram increases as water content increases. (Developed dichromated gelatin holograms can be erased by soaking in water and then drying in air.)

Chang maintains that the theory of the formation of a complex of chromium-gelatin-desiccant is refuted by c. and the observations that:

a. Dichromated gelatin holograms can have very high diffraction efficiency in a water bath before the final alcohol development.
b. Diffraction efficiency of a developed hologram rapidly decreases in a high humidity environment.

Chang proposes that the modulation produced during exposure is a hardness differential within the gelatin. When the gelatin is wetted, the hardness differential becomes a differential in the swelling of the gelatin. It is known that hardening of gelatin produces relatively large changes in swelling(58). The process of dehydration with an organic water-miscible solvent results in the displacement of water in the gelatin with solvent. The gelatin shrinks with the displacement of water with solvent and also looses plasticity. As the gelatin drys, it continues to shrink, but it cannot shrink to its original size because of the loss of plasticity. The amount of shrinkage possible is determined by the degree of swelling before the alcohol bath. Thus a small hardness differential is converted to a relatively large density differential by the swelling of the emulsion, and this density differential is "frozen" by the dehydration process.

This mechanism is supported by the loss of diffraction efficiency with absorption of water into the emulsion accompanied by a thickness decrease of 10 to 20 percent(58). It is also observed that a weak diffraction efficiency exists after exposure and before development(59).

A similar conclusion is reached by Samoilovich(60) but with additional experimental work on the behavior of hardening agents in regard to pre-hardening, sensitization, photochemical hardening, and holographic performance. Chrome alum and formaldehyde as pre-hardeners are compared. It was observed that:

-The same molar concentration of each hardener is necessary to get the same hardening as measured by melting point. However, ten times more formaldehyde is needed to obtain the same hardening as measured by swelling.

-The chrome alum is more susceptible to a dark reaction at high humidity.

-Formaldehyde hardening is reduced if the gelatin is dryed at high humidity.

-Both pre-hardeners have the same effect on photochemical hardening when measured by swelling of the gelatin.

-When the gelatin is pre-hardened to the same degree (as measured by swelling) the diffraction efficiency is the same for both pre-hardeners. However, a greater exposure is necessary when formaldehyde was used.

-In terms of absorption of sensitizer, there is no difference between the two pre-hardeners.

Sjölinder(61) presents evidence that the refractive index

modulation is the result of a chromium-desiccant-gelatin complex, and has nothing to do with hardening. This is supported by the observation that the chromium content in the gelatin resulting from photochemical hardening is not linear with the hardness of the film as measured by the solubility of the gelatin. However, the exposure at which this non-linearity is evident is far beyond the exposure usually needed for maximum diffraction efficiency of a hologram.

There is no experimental test published which measures the refractive index change resulting from dichromate-like development after hardening by some chemical means other than photochemical hardening with dichromate. Sjölinder(61) found that hardening by UV exposure resulted in a decrease in RI after development, however, UV hardening is the result of breaking bonds in the gelatin(62) and is completely unrelated to the photochemical hardening of dichromated gel.

2.3 SILVER HALIDE MATERIALS

2.3.1 Introduction

Silver halide recording materials are the most commonly used materials for scientific and display holography. Table 2.3.1-1 presents the most often used of the available materials, although the list is not exhaustive.

MATERIAL	SUBSTRATE	SPECT.SENS	SENS.(mJ/cm^2)	RESOLUTION
Kodak 649F	F&P	Pan.	.08	>2000(64,65)
Kodak 649GH	P	Ortho.	.095	>2000(64,65)
Kodak 120-02	P	640&710 nm.	.042	>2000(64,65)
Kodak 131	P	Pan.	.0024	1250(64,65)
Kodak 125	P	Ortho .	.005	1250(64,65)
Kodak SO173	F	640&710 nm.	.042	>2000(64,65)
Kodak SO253	F	Pan.	.0024	1250(64,65)
Kodak SO343	F	Ortho.	.095	>2000(64,65)
Kodak 1A	P	Ortho.	.095	>2000(64,65)
Kodak TE	P	Ortho.	.08	>2000(66)
Agfa 8E56-HD	F&P	Ortho.		
Agfa 8E75-HD	P	Pan.		
Agfa 10E56	F&P	Ortho.	.006	2500(67)
Agfa 10E75	F&P	Pan.	.005	2500(67)

P=Plate; F=Film

Table 2.3.1-1 Selection of available silver halide materials suitable for holography.

There is presently little research in silver halide holographic materials. Agfa has gone to the most trouble to bring out materials developed specifically for holography. Kodak has generally used existing materials for the holography market. Although Agfa has attempted to

cater to the holography market more than Kodak, problems such as poor quality control indicate that Agfa does not consider holographic recording materials a particularly high priority. The author feels the reason is mostly economic. The market for holographic materials is not large, and until the market expands, the major manufacturers are not likely to commit large amounts of research funds to holographic emulsion development.

As an area of research, holographic recording material is a very fertile field. There are numerous materials and processes which have been developed and optimized for the imaging market, but have not even been tried for holographic applications. Examples might be infectious development used for lithographic products and hardening chemistry used for offset printing plates. Dupont is presently developing a camera speed photopolymer system for washout lithography plates which uses silver halide developer by-products to insolubilize the polymer(68). Perhaps it would work as a phase holographic medium.

2.3.2 Development Processing of Silver Halide Materials

Silver halide materials used to produce amplitude holograms use density (more correctly amplitude transmittance) as the

modulated parameter. Because of the relatively low diffraction efficiency of planar amplitude holograms, there is less interest in holograms of this type, except for interferometry applications. However, an advantage of planar amplitude (or phase) holograms is the relative insensitivity of the hologram to distortion of the emulsion. This is due to the fact that the fringe pattern is large compared to the thickness of the emulsion, and is generally oriented nearly perpendicular to the surface of the emulsion. Therefore, fluctuation in the thickness of the emulsion has little influence on the fringe orientation. Thus, normal photographic processing where a significant volume of silver halide is fixed out causing a reduction in thickness of the emulsion, does not cause distortion of the holographic image. Volume amplitude holograms are of impractically low diffraction efficiency (theoretical 3.7 percent for transmission and 7.2 percent for reflection(69)).

As explained in Section 2.1.2, linear recording of an amplitude hologram results when the exposure range of the interference pattern falls on the linear portion of the amplitude transmittance vs exposure curve of the material. The amplitude transmittance curve can be related to the

more familiar D log H curve by the following derivation(70). In the linear portion of the D log H curve

$$\log (1/T_2) - \log (1/T_1) = \gamma (\log H_2 - \log H_1)$$

since D = 1/T where T is intensity transmittance and D is density. This rearranges to

$$\log T_1 - \log T_2 = \gamma (\log H_2 - \log H_1).$$

Substituting amplitude transmittance t for T ($t = \sqrt{T}$)

$$\log (t_1)^2 - \log (t_2)^2 = \gamma (\log H_2 - \log H_1)$$

which reduces to

$$\log (t_1/t_2) = \log (H_2/H_1)^{\gamma/2} .$$

This shows that linearity in amplitude transmittance is achieved when gamma is equal to plus or minus 2. In reality, it is only necessary that the instantaneous gamma value be 2 at the point of average exposure of the hologram; however, exposure latitude is seriously reduced if this point falls on the toe or shoulder of the D log H curve.

The area of holographic developing agents is very imprecise and difficult to summarize. Only over the last few years have the factors which contribute to successful holographic imagery been scrutinized. Developer formulations optimized

to the conditions of holographic imagery have not been fully investigated. The relevant factors which must be considered are: extremely fine emulsion grain structure, the high spatial frequency of the interference pattern, minimum emulsion distortion, minimum gelatin damage, and developed grain structure. The grain structure and density must be optimized for producing distortionless amplitude holograms or highly efficient, low noise bleached holograms.

Kodak D-19 (Appendix A) has been the work horse of holographic developers. The gamma produced by this developer is high in order to achieve linear amplitude transmittance. However, there is no reason to believe that the grain structure resulting from the solution physical development of D-19 (90 g/liter of sulfite) will be optimal either for amplitude holograms, or for bleaching.

Physical developers have received some attention but not as a system with a particular bleaching agent(75,77,83,83). Grain structure resulting from bleaching has been investigated (see below). Similar work dealing with the wide variety of developers has received very little attention(75).

Benton has used a phenidone/ascorbic acid developer with a silver halide solvent for controlled physical development (see below), but mentions that noise results from dichroic fog. There is no antifoggant or surfactant in his formulation.

Hardening developers have been found to help minimize emulsion shrinkage, and it is postulated(72) that phase modulation from the hardening action of the developer contributes to the overall phase modulation of a bleached hologram.

Other developer chemistries and methods which have been published include monobaths(94), color coupling reactions(95,96), and use of the Herschel effect(97).

The area of developer chemistry is certainly a wide open area for research. As with emulsion formulation, there exist numerous developer formulations and vast knowlege of the field, and very little of this existing knowlege has been applied to the field of holography.

Bleaching of an amplitude silver halide material converts it to a phase material and increases the achievable

diffraction efficiency. In the case of a volume transmission hologram, this increase is from a theoretical 3.7 percent for an amplitude hologram to a theoretical 100 percent for a phase hologram. For a plane hologram, the increase in theoretical diffraction efficiency with bleaching is from 6.25 percent to 33.9 percent(69). Because amplitude silver halide holograms are often bleached to convert to phase, the behavior of the emulsion during development is of particular interest.

Unlike a plane hologram, a volume hologram is very sensitive to any distortion of the emulsion, especially changes in the thickness of the emulsion. This is because the fringe pattern is small compared to the thickness of the emulsion. Also, the fringe pattern is often oriented at an angle to the surface of the emulsion, and, in the extreme, nearly parallel to the surface of the emulsion (in reflection holograms). Changes in thickness of the emulsion of a volume hologram change the orientation of the fringe pattern and the optimum play-back of the hologram is no longer at the same wavelength at which it was recorded. This change in the play-back characteristics of the hologram results in a distortion of the holographic image and a loss of diffraction efficiency.

Hardening developers have been used to reduce shrinkage of the emulsion. The accepted mechanism for the reduction of shrinkage of an emulsion developed with a hardening developer is the formation of a hardened shell of gelatin around the developed grain, which maintains the dimensional stability of the gelatin when the silver grain is bleached away(71-75). Most bleaches also harden the emulsion to some extent.

Spierings(71) describes the use of pyrogallol as a holographic developer in conjunction with an acid dichromate bleach. The degree of hardening of the developer can be controlled by the concentration of sulfite in the developer(75) and the effect is significant enough that the play-back wavelength of a reflection hologram can be controlled by the sulfite concentration. Pyrogallol causes staining of the emulsion which can be regarded as either an advantage or disadvantage depending on the application. Staining can be advantagious for display purposes because it masks noise and improves the contrast of the hologram. For HOEs, however, is is regarded as a disadvantage because of the lost diffraction efficiency. The stain can be partially removed by the acid permanganate Kodak stain remover S-13(76).

Cooke and Ward(72) indicate that pyrogallol with no restrainer causes swelling of the emulsion. They control the degree of hardening by using non-staining ascorbic acid as a restrainer, and suggest a peroxide bath to further reduce stain.

Lamberts and Kurtz(76) suggest the use of catechol in conjunction with a reversal bleach to reduce emulsion shrinkage. Catechol is also described by Cook and Ward(72) as a good developer for reflection holograms in conjunction with a p-benzoquinone bleach. It produces minimal shrinkage and results in no stain.

Benton(77,81) introduced a solvent developer, called PAAP, which uses ascorbic acid as a developer, phenidone as an accelerator and ammonium thiocyanate as the silver halide solvent. Because of the high spatial frequency of the fringe pattern, it is possible to diffuse silver halide from the unexposed areas between fringes to the adjacent exposed fringe areas. Proper balance between exposure and solvent concentration results in the complete transfer of unexposed silver halide to the exposed sites, and obviates the need for fixing. Emulsion shrinkage is minimized since there is little net loss in the volume of solids within the

emulsion. The method suffers from noise caused by scatter introduced by dichroic fog.

Swelling agents have been used to control the thickness of the emulsion. Linn(78) used 5 - 10 percent triethanolamine in alcohol to swell the emulsion after development. It has been reported to be difficult to maintain surface uniformity with this method(77,72).
The grain size distribution of the emulsion is significant, not only in view of the resolution of the material, but also relative to its effect on emulsion deformation. The smaller the grain size, the less disruption of the emulsion during development and fixing, and the more receptive it is to solution physical type development. Also, there is less scatter and absorption of radiation during the exposure of the hologram. The trade off is, of course, lower sensitivity.

Another interesting aspect of grain size was reported by Usanov (79). He found that if the grains in an emulsion were of average diameter from 20 - 50 nm, and the average number of particles was greater than 55 particles per cubic micron, then the emulsion showed a refractive index modulation rather than a transmittance modulation. The RI

modulation was dependent on the grain diameter over the range above.

2.3.3 Bleach Processing of Silver Halide Materials

The subject of bleaches for holography is widely discussed in the literature, with very little agreement. Phillips' opinions(84) regarding the factors important for different types of bleaches illustrate the types in use and possible relevant parameters in the use of bleaches. Phillips indicates that the gelatin hardness, the fineness of grain, the preservation of the grain-gelatin interface during bleaching, the hardening action of the bleach and the granular coagulation of silver halide during bleaching are important factors influencing the success of a bleach.

Some of these factors would also be influenced by the developer used and could be summarized as the grain structure and gelatin condition left by the developer.

A solvent bleach, such as acid dichromate, is used to dissolve away the silver of a developed hologram, leaving the unexposed silver halide as the modulating material. This method is referred to as a reversal bleach. For dichromate, some tanning also results from reversal

bleaching, which may contribute to modulation. The combination of tanning and leaving the unexposed and undisturbed silver halide in the emulsion, minimizes shrinkage of the emulsion and reduces noise from scatter. Phillips feels that the high acid concentration of acid dichromate will damage the gelatin, eliminating the beneficial tanning effect of the developer. The solvent bleach will also dissolve out silver halide (as well as silver) and reduce modulation. Potassium permanganate and ceric acid can also be used as solvent bleaches but Phillips feels these are much too damaging to the gelatin.

A solvent developer can also dissolve out silver halide and work against a reversal bleach. If a coarse grain structure is left by the developer, deformations of the gelatin caused by the grain structure will be retained, especially by a hardening solvent bleach. Increased scatter will result.

A rehalogenation bleach oxidizes developed silver to a silver halide or a transparent silver salt. Bromine water, iodine in alcohol, potassium ferricyanide, mercuric chloride, and ferric nitrate with potassium bromide are used. Phillips finds that irregular grain growth or

clumping during bleaching (caused by coagulation of grains or increases in crystal dimension over that of silver) cause severe scatter. Phillips says gelatin damage is a problem with bromine, potassium ferricyanide, and mercuric chloride. Lehmann(86) used phenosafranine with ferric nitrate and Phillips says that this acts as an anticoagulant.

Phillips introduced the bleach p-benzoquinone(PBQ) for holography(84). The advantages of PBQ are:
a. It has a similar structure to developer oxidation products and, therefore, should not destroy developer hardening of the emulsion. b. It has a pH range of 1-9.5.
c. It does not destroy developer stain (this is mostly important for display purposes).
d. There is low release of free bromine.
e. There is low solution of silver bromide from the emulsion.
f. It is a tanning bleach and the tanning can be controlled by pH and the addition of chromium ion.

This bleach has become very popular in the holographic community.

Joly(74) has investigated grain growth during rehalogenating bleaching. A model for scattering phenomena in bleached emulsions has been presented by van Renesse(85).

2.3.4 Tanning Development of Silver Halide Materials

Tanning developers have been used in many applications, among them the Jos Pe Process, the Duxochrome Process, the Kodak Dye Transfer Process, the Technicolor Imbibition Process(87), and lithographic printing(88).

The mechanism of the tanning action of developer by-products with gelatin involves the cross-linking of amine groups present in the gelatin(89). A representative reaction is illustrated in Figure 2.3.4-1 which shows the probable reaction of the catechol developer oxidation product with gelatin.

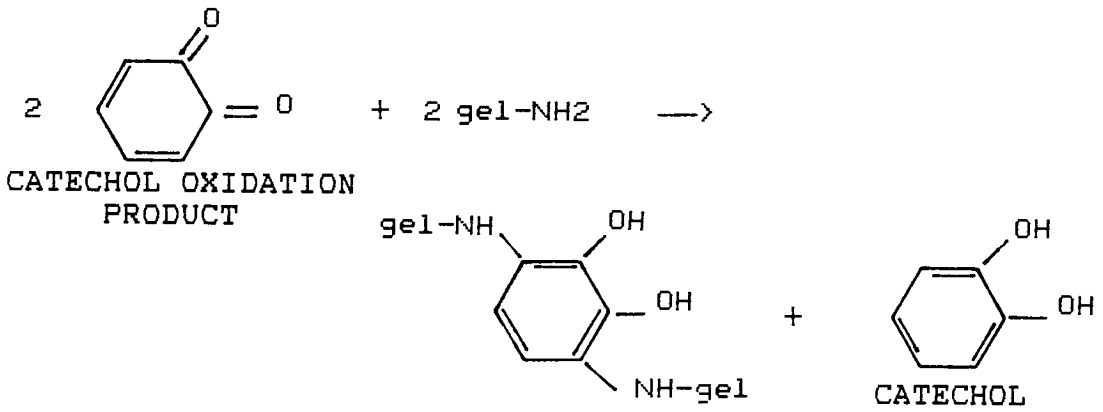


Figure 2.3.4-1 Probable reaction of catechol developer oxidation product with gelatin.

Tull(90) has written an excellent review article on tanning development. The best tanning agents have two or more hydroxyl groups. Developing agents with only one hydroxyl group are generally moderate to weak tanning agents, and those with no hydroxyl groups show no tanning action. Certain combinations of developers show superadditive effects; for example, metol with the tanning developers pyrogallol, tannic acid, hydroquinone, catechol, or gallic acid shows greater tanning than the tanning developer alone. Other combinations, such as the tanning developer pyrogallol and hydroquinone, show less tanning action than

the tanning agent alone.

Pontius(91) suggests that the behavior of combinations of developers could be explained by the oxidation potentials of the developers and their oxidation products. Metol would be more readily oxidized by silver bromide than, for example, pyrogallol, and its oxidation product could promote the oxidation of pyrogallol. Pyrogallol, however, would be more readily oxidized than, say, hydroquinone, and some of the pyrogallol oxidation product would be consumed in oxidizing the hydroquinone.

Tull(90) found that, in fact, almost any developing agent used without sulfite would tan, if an oxidizer such as ferricyanide was used following development. Ferricyanide bleaches the developed emulsion, but is not itself a tanning agent. Sulfited developing agents followed by an oxidizer showed no tanning action. In general, almost any oxidizer will increase tanning action; however, some developers work better with certain oxidizers.

Tull found that the relationship between the amount of tanning and the silver density following development varied widely depending on the type of developer, the pH of

development, developer concentration and the presence of a post-development oxidation bath. It was observed that:

a. For a given pH, the higher the developer concentration the lower the resulting tanning for a given silver density.

b. In some cases, strong tanning action was observed with very little visible silver density.

c. Lower temperature produced less silver density but greater tanning.

d. Increasing the time of development increased the silver density contrast but the tanning effect remained constant in contrast and increased in overall tanning.

e. Increasing the time of the oxidizer bath resulted in increasing tanning action.

Tull proposed that the initial effect of tanning development is the laying of a foundation of gelatin-attached developer residue. Minimum development time is that required to lay this foundation. The actual tanning action then proceeds by an independent mechanism of uniform rate over the whole image, independent of the development of the silver image.

Increasing the wash time before the oxidizing bath was found to encourage hardening action, even for long

oxidizing bath times. This was an unexpected and unexplained result.

The method used by Tull included an acid stop bath and a fix bath. It was observed that if these baths were eliminated, but the oxidation step used, increasing wash times resulted in, first, a decrease in hardening, then an increase. Interference by residual developer was established and interference by the presence of silver halide was postulated.

Tull found that the oxidizing bath could be replaced with an alkali bath with very similar results.

There was evidence that the tanning action of the developer and stain formation in the gelatin were not related and proceeded by separate mechanisms. Presumably, staining is the result of the reaction of the oxidized developer with an unoxidized developer molecule.

3. INTRODUCTION TO PRESENT WORK

The premise which the present work seeks to test is that it is possible to devise a silver halide emulsion for holography which will result, after processing, in a hardening modulated hologram. The hardening modulated hologram may then be convertable to a phase hologram by dehydration of the gelatin with alcohol. The phase modulation would be the result of a refractive index modulation within the gelatin, analogous to the modulation resulting from the dichromated gelatin process.

In the dichromated gelatin process, image-wise hardening results from the photochemical reaction of dichromate ion with gelatin. If a hardening developer is used, an image-wise hardening of the gelatin will take place in the vicinity of developed silver halide grains. If the development and hardening conditions are designed to duplicate the conditions of the hardening of dichromated gel, subsequent sudden dehydration with alcohol may result in an index modulation similar to that of dichromated gel.

Cook and Ward(72) describe a development process designed for reflection holograms which uses a hardening developer (catechol) and a hardening bleach (p-benzoquinone). They

recognize the parallel between the hardening chemistry and dichromated gelatin, and experiment with an alcohol dehydration. They find that the alcohol treatment swells the emulsion and, therefore, changes the play-back angle. With proper correction for boundary reflections at the new play-back angles, an apparent increase in diffraction efficiency is seen. This could indicate that the hardening differential introduced by hardening development is converted to phase modulation by the alcohol bath. The effect is more pronounced at lower exposure levels than high, but some improvement is seen in peak diffraction efficiency. It is pointed out that the increase in efficiency at lower exposures may have been more the result of emulsion swelling than increased modulation. This is because at lower levels of modulation, the increase in Bragg angle would improve efficiency. At higher levels of modulation the Bragg angle change should have no effect.

Chang and Winick(39) describe the use of a dichromate solvent bleach on a normally developed silver halide emulsion, followed by fixing and an alcohol bath to obtain a dichromate-like hologram. A hardening developer is not used in this case. The hardening action of the dichromate bleach is apparently converted to a refractive index

modulation by the alcohol bath.

To produce holograms from silver halide material, a very fine grain emulsion is desirable. Fine grain provides obvious advantages in resolution. Also, fine grain structure leads to minimal disruption of the gelatin during development and fixing, resulting in minimal distortion of the emulsion and introduction of scatter. Since the objective of a hardening developer is hardening action rather than density, grain growth during development can be kept to a minimum, taking maximum advantage of the initial fine silver halide grain structure.

Tull(90) shows that significant hardening action can take place with minimal grain growth, especially if an oxidizing post-development bath is included. It is expected, however, that some development of density would be necessary to obtain the necessary hardening action.

A low silver halide concentration in the emulsion is expected to be advantageous for minimizing emulsion distortion and scatter. There will be a trade-off, however, between minimum silver halide content and acceptable emulsion sensitivity and resolution.

To maximize the resolution of hardening and keep the method as parallel as possible to the dichromate process, the developer can be incorporated into the emulsion, and development initiated by a change in pH of the emulsion. This avoids swelling the emulsion during development. The compact molecular structure of an unswollen emulsion will decrease the migration of the developing agent, increasing the resolution of the hardening action. Also the close proximity of the gelatin molecules will encourage cross-linkage and hardening. Lowering the temperature of the developing step would be expected to further encourage hardening and discourage silver grain growth as mentioned by Tull(90).

Yackel(92) describes the use of a hardening developer (4-phenyl catechol) incorporated into a silver halide emulsion. The developer is insoluble at mid pH values and soluble at higher pH. The objective of Yackel's work is to produce high resolution relief images by differential hardening and warm water etch of the emulsion. The developer is advantageous because it is stable, exists in the emulsion as very fine crystals, can be released by raising the pH of the emulsion, and is relatively immobile due to the phenyl "tail" on the developer molecule. This

developer is also described by Yackel and Abbott(88) for use in a silver halide emulsion for lithographic printing plates.

To optimize the geometry of the gelatin for hardening, the emulsion can be developed in the unswollen state. Smith(93) describes a method for real time holography for interferometry which uses an experimental emulsion with an incorporated developer. The film is developed in situ by raising the pH of the emulsion with ammonia or methylamine gas. Methylamine is preferred due to the attainment of a higher maximum density of the developed film. This method is used to produce amplitude type holograms.

The emulsion can be precipitated in photographic bone gelatin to take advantage of the known behavior of this gelatin(104). However, the emulsion can be diluted with acid processed pig gelatin to take advantage of the fact that the pig gelatin is richer in amine groups (isoelectric point about 9) than bone gelatin (isoelectric point about 4.8)(104). Since the hardening action of developer oxidation products involves the cross-linkage of amine groups, the pig gelatin is expected to be more sensitive to hardening by developer oxidation products than bone

gelatin.

An oxidizing bleach following development is expected to be advantageous to promote hardening of the emulsion(90) and convert developed silver to silver halide for removal in a subsequent fix bath. p-benzoquinone is proposed as the bleaching agent, due to its activity over a wide pH range, and its reported advantages in non-destruction of emulsion hardening and subsequent low introduction of scatter(84). The intention is to use the bleach at the same pH as the emulsion (pH = 5 to 6).

The silver halide remaining in the emulsion can be fixed out with a thiosulfate fix bath. If no general hardening (bias hardening) is desired, a non-hardening fix such as Kodak F-24 (Appendix A) can be used. If bias hardening is desired, a hardening fix such as Kodak F-5 (Appendix A) with varying amounts of potassium alum can be used.

Final refractive index modulation would be achieved by isopropanol baths as normally used in dichromated gel development (described in Section 2.2.1).

4. METHODS

4.1 THE EMULSION

4.1.1 Precipitation

The emulsion used is modeled after a fine grain Lippmann emulsion described by Berry and Skillman(101). A double jet precipitation is described using silver nitrate and alkali halide solutions of equal molar concentrations. 1-phenyl-5-mercaptotetrazole is used as a grain growth inhibitor. The method works well for silver bromide or silver bromoiodide emulsions if the iodine content is kept low. Grain size from less than 10 nm. to 30 nm. is claimed.

Ten percent phthalated gelatin was prepared as per(100) so that the fine grain emulsion would coagulate properly during washing.

As the exposure of the holographic emulsion was to be done with the 488 nm. line of an argon laser, a three mole percent silver bromoiodide emulsion was used. The absorption coefficient of a silver bromoiodide crystal containing 3 mole percent silver iodide is over $100cm^{-1}$ at 488 nm.(103). This was found to give sufficient sensitivity to exposure at 488 nm. and thus avoid the complication of

spectrally sensitizing the emulsion to red.

The preferred grain growth inhibitor in Berry and Skillman's patent is 1-(dicarboxylphenyl)-5-mercaptotetrazole, the carboxyl groups acting as solubilizing groups. As this compound was not commercially available, 1-phenyl-5-mercaptotetrazole was used.

In the emulsion precipitation 90 ml. of a 1.962 mole per liter silver nitrate solution, and 90 ml of a 1.901 mole per liter potassium bromide plus .0588 mole per liter potassium iodide solution were added simultaneously to 1200 ml. of 0.44% photographic grade bone gelatin containing 0.05 mole per silver mole of 1-phenyl-5-mercaptotetrazole (1.5734 g.). The pAg of the gelatin mixture was first adjusted to 8 to ensure an excess of halide. Addition was over 12 min. at 34°C. The emulsion was washed by coagulation in the usual manner(102). A significant deviation from the original patent was made in order to be able to wash by coagulation. The concentration of the bone gel solution into which the emulsion was precipitated was reduced by a factor of 10 to effect successful coagulation. This caused no apparent ill effects.

The coagulate was centrifuged to effect sufficient separation from its supernatant liquid so that photographic grade acid processed pig gelatin could be added to give a final concentration of 0.005 mole Ag per gram gelatin. The pH was adjusted to 6.

The final emulsion contained 20 to 25 percent bone gelatin and no problems with coacervates were encountered. 0.33 grams of thymol per gram gelatin was added as a preservative.

The silver concentration of 0.005 moles of silver per gram of gelatin is based on expected concentrations needed to obtain density in the developed emulsion(104). In terms of resolution, the minimum period recorded at 488 nm. would be $\lambda/2$ = 244 nm. If an average grain size of 20 nm. is assumed and 2 grains are needed along each dimension to record this periodicity, the silver concentration needed is 0.00015 moles per gram of gelatin. At five grains per period, the silver concentration would be 0.0025 moles per gram of gelatin. The actual minimum silver concentration needed for the process is impossible to predict, but it was felt that 0.005 moles per gram gelatin was high enough to assure adequate tanning action and resolution.

Although no quantitative measure of grain size distribution was made, a sample of the emulsion was developed and inspected under a 1500X microscope. No grain was visible. Given the angular resolution of the eye to be 1 arc minute and the magnified image of the microscope to be at 25 cm. from the eye, grains as small as 0.046 micron would be resolvable. The absence of visible grain was deemed sufficient evidence that the emulsion had fine enough grain structure to continue the investigation.

4.1.2 Chemical Sensitization

To determine correct conditions for sulphur-gold sensitization, a series of sensitometric exposures at five minute intervals of blotting paper dipped in a portion of the emulsion was run. Each series contained a varying amount of sensitizer. These strips were developed in Kodak HC 110(diluted to 11% from stock).

It was expected that the concentration of sulphur-gold sensitizing solution needed would be higher than is normal in the art because of the large grain surface area and the presence of the grain growth inhibitor(104). Indeed, it was found that to achieve optimal chemical sensitization at 60°C in a time of 40 minutes, 50 mg. per silver mole of

thiosulfate, 10 mg. per silver mole of potassium auro chloride and 100 mg. per silver mole of potassium thiocyanate were necessary. No fog was detected even at 60 minutes. This indicates a very low degree of developability of the emulsion.

No useful indication of speed was obtained from these tests. Exposure was 30 flashes from a Kodak 101 sensitometer which could give no quantitative indication of speed except to say it is extremely slow compared to even the slowest camera films.

4.1.3 Developer Incorporation

The incorporated developer was initially added directly into the emulsion. A 10% solution of 4-phenyl catechol in methanol was delivered into an emulsion sample at a rate of 5 ml. per minute with strong stirring. A rubbery precipitate formed immediately. This problem was solved by precipitating the developer separately and adding it to the emulsion. The method of incorporating the developer was developed during the course of the experimentation with the following problems and solutions:

-The developer precipitate was too large, and dropped to the bottom of the beaker. A colloid which did not settle

was obtained by precipitating into a 1.0% solution of bone gel at 0°C, and by reducing the methanol content in the final developer slurry. This was done by increasing the concentration of the developer in methanol to 20%, and by increasing the volume of the 1.0% bone gelatin solution into which the developer was precipitated. The maximum limit of this volume is determined by the desired dilution of the emulsion for coating and/or the amount of additional bone gelatin allowed into the emulsion, as this solution can be used to dilute the emulsion at coating. Present work did not take full advantage of this fact. The minimum developer concentration actually used in the slurry was 0.075%. The minimum possible was 0.0075%, given the coating conditions used, but the amount of bone gelatin introduced at coating would have increased by a factor of ten, bringing the final emulsion to about 50% bone gelatin. The developer grain size worsened as the precipitation progressed suggesting a ripening effect, and decreasing the methanol concentration served to lower the solubility of the developer. The rate of delivery of the developer in methanol solution ended up to be about 5 ml. per minute. -The developer precipitate was very susceptible to air oxidation, evidenced by a brown gelatinous layer being

formed on the top of the stored developer colloid. The immediate danger of loosing the whole batch of emulsion was solved by adding the developer colloid immediately before coating. Precautions such as storing under refrigeration and minimizing any air gap above the stored precipitated developer did not eliminate the problem, and the developer colloid was beyond use in as little as 15 days.

The initial concentration of the incorporated developer chosen (42.468 g. per silver mole) was that indicated by Yackel's patent(92) to have optimal keeping qualities and adequate density.

4.1.4 Coating

A final emulsion thickness of about 10 microns was desired. To determine coating weight, account was taken of the volume of both the gelatin and the silver halide at the silver halide to gelatin ratio used. It was found that the best results were obtained when a sample of emulsion was diluted to 1.2% gelatin (the developer colloid was added at this time), heated to 45°C and puddled onto a subbed 5 cm. X 7.5 cm. glass microscope slide warmed to approximately 50°C by placing the plate on a warm surface. The emulsion

was distributed with a glass rod. In the initial experimentation, 1.5×10^{-4} grams formaldehyde per gram of gelatin was added before coating as a prehardener, as well as 0.75 grams saponin per liter of emulsion as a wetting agent(105).

The large volume and slow drying of the plate left a characteristic pattern in the final coated plate (Figure 4.1.4-1)

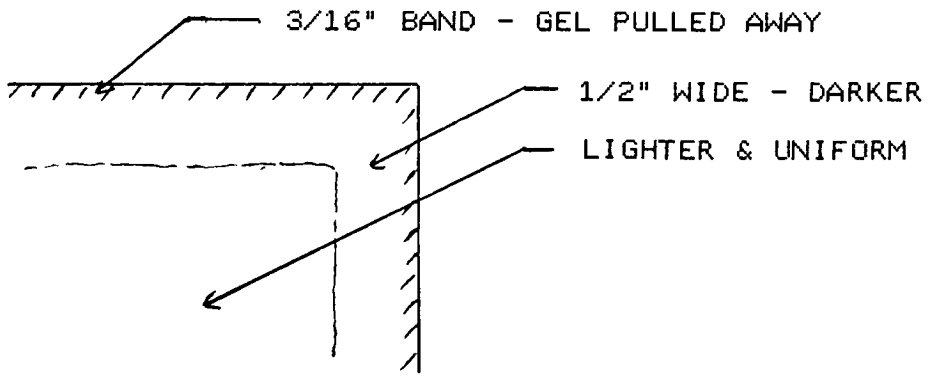


Figure 4.1.4-1 Emulsion pattern on a dry coated plate.

Exposures were made in the central, even area of the plates.

The method of subbing was obtained from Mr. H. Roberts and is included in Appendix B.

A bias hardening was initially thought to be necessary but the amount was unpredictable, especially since no previous work had been done with pig gelatin. It was desired to harden the emulsion during coating just sufficiency to give

it resistance to dissolving in the processing baths.

The choice of the prehardening reagent and its concentration was based on the work of Samoilovich(60). He found that formaldehyde was less susceptible to a dark reaction with storage and it was chosen for this reason. The concentration intended to be used (1.5×10^{-4} grams per gram gel) was one tenth of the concentration found by Samoilovich to give maximum diffraction efficiency with the dichromate process. It was also about a tenth of the concentration recommended by Yackel(92) to slightly harden an emulsion with poor physical characteristics when an incorporated hardening developer is used. Through error, the amount actually added was 1.5 X 10-3 grams per gram gel, a factor of ten higher than intended, and equal to the recommendations of Samoilovich and Yackel. This error was consistent through the work.

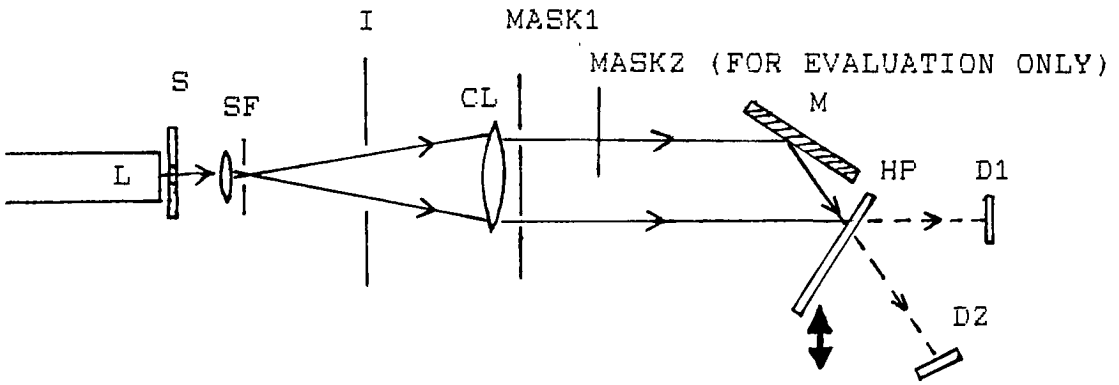
4.2 EXPOSURE

A number of exposures to evaluate the response of the material to exposure and processing were made using incoherent light. These exposures were made with a high intensity lamp bulb about six inches from the test plate. The test plate was exposed through a step tablet with density increments of about 0.15. An exposure time of two minutes gave satisfactory density with reasonable developing times (to be discussed later). The objective was not to characterize the material in white light, and no absolute measures of irradiance were made.

Grating exposures were made at 488 nm. with a Coherent CR-2 argon laser equipped with a wavelength selector and etalon available through the Tech-Photo Department.

The optics arrangement used is illustrated in Figure 4.2-1.

A.



B.

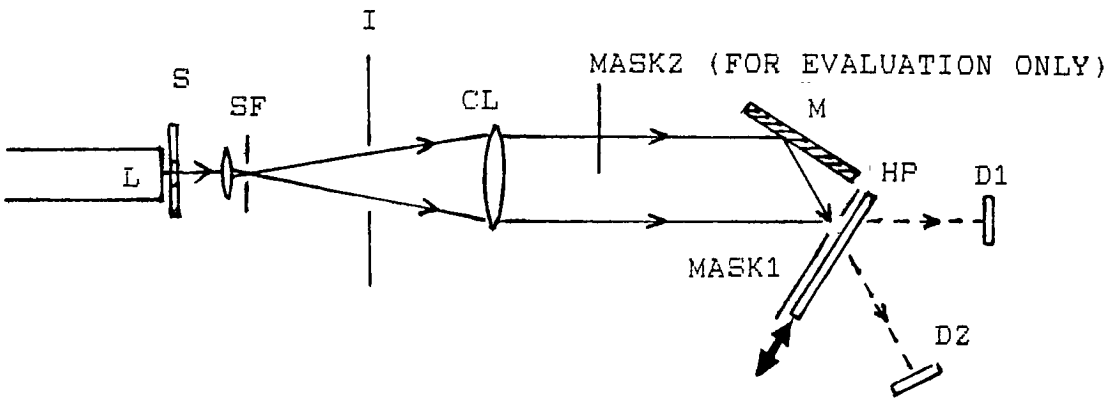


Figure 4.2-1 Optical setup for exposing and evaluating test holographic plates.

L = laser
SF = spatial filter (40X objective, 25 micron pinhole)
I = iris
CL = collimating lens
M = front surface mirror
HP = holographic plate
D = detector
S = shutter

The power distribution of the laser beam was assumed to be

Gaussian. The collimating lens intersected approximately the central third of the spread beam to assure a relatively low falloff of the beam intensity over the surface of the collimating lens.

The collimating lens was clean, however, not well corrected. This was acceptable since the evaluation of the holographic plate was done with exactly the same beam that was used to expose the plate.

The mirror (M) and holographic test plate (HP_1) make up a Lloyd's mirror configuration for exposing the test plate. An enlarged view of the arrangement is shown in Figure 4.2-2.

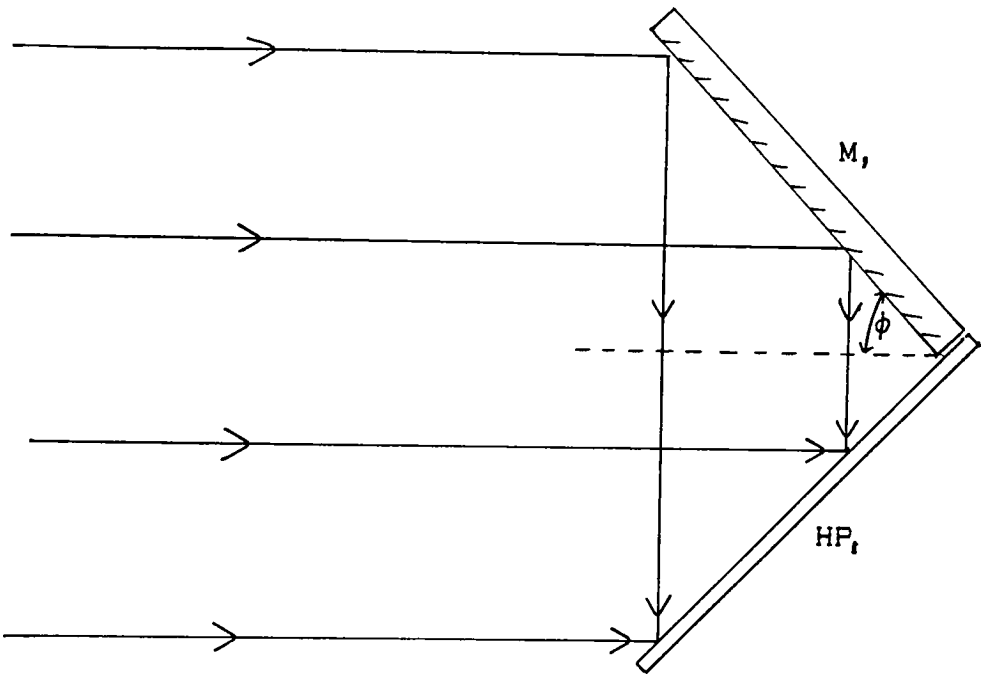


Figure 4.2-2 Lloyd's mirror exposure configuration.
HP_1 = holographic test plate
M = mirror

The Lloyd's mirror configuration was chosen because of its simplicity and because, with this configuration, the angle of incidence of the object and reference beams is always the same and is equal to the angle $(90-\phi)$ (Figure 4.2-2). This angle is easily adjusted by rotating the whole configuration. With equal angles between the object and reference beams, the interference fringes are always perpendicular to the surface of the emulsion, and the complications introduced by shrinkage of the emulsion during processing are minimized.

The angle ϕ initially was 45 degrees resulting in a grating of 2900 lines per millimeter. This was modified after the first exposure to a 15 degree incidence to obtain 1000 lines per millimeter and thus, hopefully, increase the chances of initial success with the material. The configuration was aligned by adjusting the retro-reflection back onto the pinhole of the spatial filter. The incident power on the holographic plate was taken as twice the power at the center of the collimated beam. This assumes no falloff over the diameter of the collimated beam, and no losses in reflection from the mirror.

For the bulk of the coherent exposures, a mask was placed immediately after the collimating lens as illustrated in Figure 4.2-1A and the test plate was moved in the direction of the arrows to obtain a series of exposures on the test plate. The mask position and plate movement was modified late in the work to that illustrated by Figure 4.2-1B.

Detectors D_1 and D_2, were high quality photodiodes (EG&G UV100BG)with separate operational amplifiers (Archer TLC271) and a switching arrangement so the detector circuits could be read in succession by a voltmeter.

For evaluation, Detector D_1 was first read without the test plate in position to determine the incidence power. With the plate in position, detector D_1 was read again to measure the zeroeth order beam and detector D_2 read to measure the diffracted beam. To read detector D_2, mask MA_2 must first be put in place to block the light falling on Detector D_2 from the laser.

The calculation of diffraction efficiency took into consideration losses due to the reflections within the holographic plate. Figure 4.2-3 illustrates the interference of the object and reference beams, both at θ_1 incidence, in a holographic emulsion. If the refractive index values are n_1=1.0(air) and n_2=1.62(emulsion)(99), then the interference pattern is formed from the interaction of two beams at an angle θ_2 to the normal. Although these refractive index values are actually for the Agfa 8E56HD holographic plate, it was felt that the values for the emulsion and glass used in this experiment were similar, and reflectance values based on these figures would be valid.

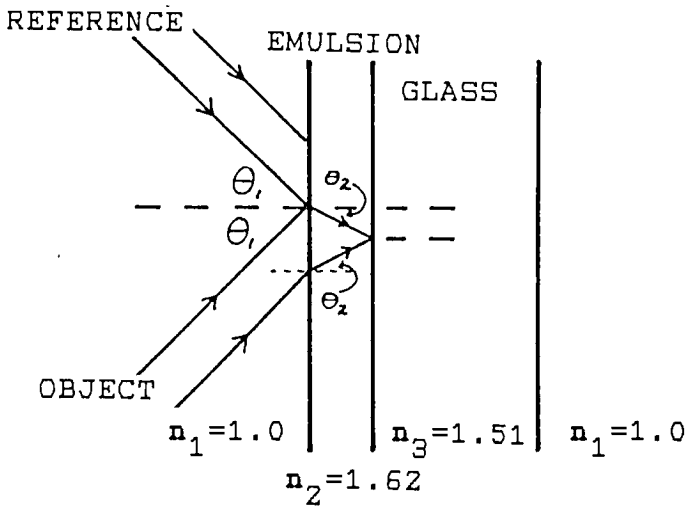


Figure 4.2-3 Diffraction of the object and reference beams when entering the emulsion.

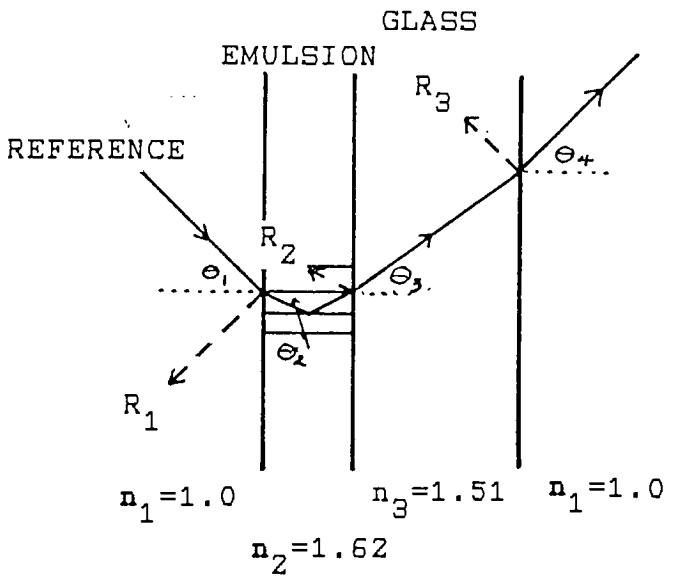


Figure 4.2-4 Diffraction and reflection of the reference beam during reconstruction of the hologram.

Figure 4.2-4 indicates the reflections resulting when the hologram is reconstructed with the reference beam. The

glass refractive index is assumed to be 1.51(99). The angles involved can be calculated using Snell's law. The reflectance, R, at each boundary can be calculated using the Fresnel equation for reflection of light polarized perpendicular to the plane of incidence:

$$R = [(n_1 \cos\Theta_1 - n_2 \cos\Theta_2) / (n_1 \cos\Theta_1 + n_2 \cos\Theta_2)]^2$$

The loss due to scatter and absorption was calculated by summing the powers of the zeroeth order and the diffracted beam, and finding the difference between this value and the corrected incident beam power.

4.3 PROCESSING

4.3.1 Development

A chamber was constructed for developing the plate in methylamine gas. The final configuration used is illustrated in Figure 4.3.1-1.

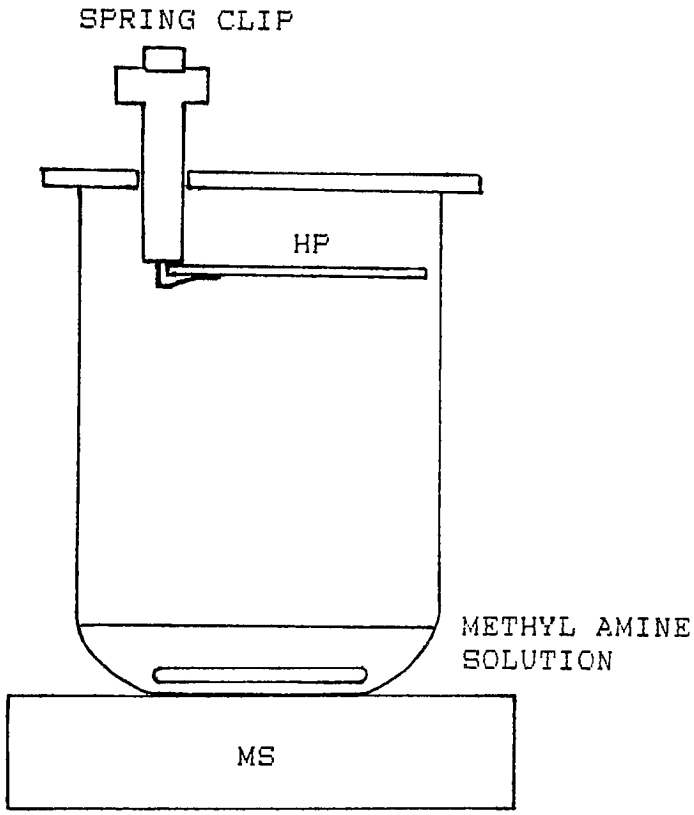


Figure 4.3.1-1 Development chamber.
HP = holographic test plate
MS = magnetic stirrer

Development temperature was room temperature. A magnetic stirrer was chosen which was least likely to heat the

methylamine solution. The horizontal position of the plate gave the most even development. Stirring was necessary and had to be slow to prevent splashing. Development took place under a red safe-light, and the appearance of density could be monitored visually. Development could be stopped by opening the container and plunging the plate into the developer wash bath.

Methylamine gas was chosen to raise the pH of the emulsion because it has been proven more effective than ammonia for this purpose(93). Ammonia was also tried.

4.3.2 Developer Wash Bath

The developer wash bath was intended to stop development and to dissolve the incorporated developer from the emulsion. As the developer is insoluble at lower pH, it was assumed a water miscible organic solvent would be necessary to dissolve out the developer. Specifics are further discussed in Section 4.4.

4.3.3 Bleach Bath

The bleach bath consisted of(84):

2 g. p-benzoquinone
30 g. potassium bromide
1.5 g. boric acid
make to 1 liter with distilled water

The p-benzoquinone (PBQ) bleach was chosen because of its success as a low scatter bleach for holography(84).

The time used for this step varied and was based on visual observation of reduction of density.

4.3.4 Hardening Fix Bath

The fix bath used was standard Kodak F-5 hardening fix:

Sodium Thiosulfate (Pentahydrate)	240.0 grams
Sodium Sulfite (Anhydrous)	15.0 grams
28% Acetic Acid	48.0 milliliters
Boric Acid Crystals	7.5 grams
Potassium Alum, Fine Granular (Dodecahydrated)	15.0 grams
Water to make	1.0 liter

This step was intended as the primary control of the important bias hardening parameter. The hardening differential between the bias hardening and the hardening by the developing agent is thought to contribute to the refractive index differential in the final emulsion. Too little bias hardening may lead to noise in the finished hologram, too much to poor diffraction efficiency (see

Section 2.2). The concentration of the alum was intended to be the controlling factor, the fix time being kept constant.

The clearing time was determined to be 30 seconds. A two minute fix time was chosen to ensure adequate removal of halides.

4.3.5 Water Wash Bath

Wash was in slowly running water for 2.5 minutes followed by a distilled water wash for 30 seconds.

4.3.6 Dehydration

The plate was dehydrated by immersion in a 50% isopropanol bath for 30 sec. and then in 100% isopropanol for 30 sec. The plate was dried at room temperature. These are common dehydration parameters used for the dichromated gel process (Section 2.2).

5. RESULTS

5.1 INITIAL OBSERVATIONS

The emulsion on which initial observations were made had the following relevant parameters:

10-30-86	Date Precipitated
42.5	Moles developer per silver mole
0.0044	Moles AgH per gram gelatin
75	% pig gelatin
25	% bone gelatin
NO	subbed plates
0.0015	grams formaldehyde per gram gelatin

Crude tests were initially run which confirmed that the emulsion, if exposed, was indeed developable by raising the pH (in this case with sodium hydroxide solution), and not developable if not exposed. Initial attempts at exposure, development, and processing of the plates were then undertaken.

The first exposure was a grating with the CR-2 laser. Development was over a 40% solution of methylamine, and the developer wash was a 10% methanol solution. Further detail in describing values and experimental conditions is either unknown or of little value since nearly all fixtures were in early stages of development. Even so, much useful information was obtained about the recording system:

- Exposure related density was obtained with methylamine gas development. This established that the available

laser power and the emulsion speed were sufficient to proceed with the work.

-Existence of a grating was detected, in this case a density grating on an unfixed plate. This grating was at 2900 lines per millimeter which indicated sufficient resolution of the emulsion.

-A subbing layer was necessary. The emulsion peeled off the plate as soon as it was placed in the developer wash solution.

With the remaining plates, a number of incoherent exposures were made to gain further information about the behavior of the emulsion. The peeling provided an easily observable test parameter which was established to be directly related to development, and presumed to be related to emulsion hardening. Table 5.1-1 summarizes the test results.

EXPOSED	DEVEL. WASH	DEVELOPED	DEVEL. WASH	OBSERVATION	DEVEL. BYPRODUCT
N		N	Y	NO PEEL	N
N		Y	Y	SLOW PEEL (10MIN)	Y
Y		Y	Y	FAST PEEL (<60SEC)	Y
Y		N	Y	NO PEEL (1HR)	N
Y	Y	Y	Y	SLOW PEEL (30SEC)	Y

Table 5.1-1 Summary of incoherent exposure tests.
Y = yes
N = no

When the emulsion peeled, it swelled laterally, increasing in size by 20% to 30%. No thickness measurements were

made.

In terms of peeling, a water wash had the same effect as the 10% methanol wash, so apparently the wetting of the emulsion was the critical factor.

Developer byproduct was observed as a straw color in the developer wash solution. It was observed to only be present if development occurred, and to be stronger if density was seen.

In the last case of Table 5.1-1 where the plate was prewashed in 10% methanol before development, the "slow" peel is relative to the area of the same plate with no prewash, which peeled in about one second. Also, the prewashed area did show some density, although less than the area with no prewash.

In the instance where the plate was developed with no exposure, no density was observable on the plate.

Ammonia gas and sodium hydroxide solution were also tried as development inducers, and the emulsion behaved the same as in Table 5.1-1 for each. The visual appearance of the

density was different for the ammonia than the methylamine and may indicate that both are undergoing some solution physical development. This is not surprising, given the fact that silver forms soluble amine complexes.

The behavior of sodium hydroxide as a development inducer is further discussed in Section 5.5.

5.2 OBSERVATION OF DEVELOPER BYPRODUCT GRATING

Based on the initial use of the equipment, several changes were made. The developing vessel and exposure optics were brought to the conditions described in Sections 4.2 and 4.3.

The initial observations led to the conclusion, besides the need for subbing, that the developing (and thus hardening) action was too strong. Non specific development was apparent. Also, the developer wash step did not appear to be effectively removing the incorporated developer from the emulsion.

Based on these conclusions the following changes were made:

- -The plates were subbed.
- -The incorporated developer concentration was halved.
- -The concentration of the methylamine solution used in the developing vessel was reduced from 40% to 10%.
- -The developer wash step was changed to two 20 ml. baths in 90% methanol.

The emulsion used in this section had the following relevant parameters:

1-11-86	Date Precipitated
21.25	Moles developer per silver mole
0.0005	Moles AgH per gram gelatin
80	% pig gelatin
20	% bone gelatin
YES	subbed plates
0.0015	grams formaldehyde per gram gelatin

Initial trials showed the emulsion did not peel, even under the conditions used in the initial tests. This allowed the continuation of the establishment of starting parameters for the remaining processing steps, and a series of exposures were made to accomplish this.

It was established that the two step developer wash prevented further development after removal of the incorporated developer.

Table 5.2-1 summarizes the most efficient grating obtained on each of four plates exposed with a grating exposure series.

PLATE NO.	DEVELOP TIME (MIN)	EXPOSURE (mJ/cm2)
10	15* PLUS 5¥	4.2
11	3.75	11.7
13	10	27.0
14	5	25.2

	********** GRATING EFFICIENCY **********					
PLATE NO.	Ag ONLY (%)	DEHYD. Ag ONLY (%)	BLEACHED (%)	NO Ag (%)	DEHYD. NO Ag (%)	NO Ag SCATTER + ABSORPTION (%)
10	0.7	0.7	NA	NA	NA	NA
11	X	0.3	NA	NA	NA	NA
13	X	X	22	<1.0%	<1.0%	X
14	NA	NA	NA	X	0.14	1.2

Table 5.2-1 Efficiency results for various grating exposures and processing.
* no stirring of the methylamine solution
¥ with stirring
X not measured
NA not applicable

In this series it was attempted to establish a consistent developing time, however, density obtained was not reproducible and the developing time was generally determined by the density observed. It was decided to stop development at 10 minutes or before the lowest exposure showed density, whichever came first. In this manner the range of density obtained started at zero and went up.

The most likely explanation for the irreproducible development was the sensitivity of the developing process to stirring of the methylamine solution. This sensitivity is illustrated by the developing times recorded in Table 5.2-1 for plate 10.

Plates 13 and on received an increased exposure because the early plates did not show a strong enough density range, and it was not considered desirable to raise the development time. The low density was, presumably, because of the decrease in the incorporated developer concentration in the emulsion.

In these exposures, a significant amount of density was observed in the unexposed areas of the plate. It was determined that the origination of the density was the coherent exposure of the grating. Subsequently, when the exposure station was moved to the CIS holography lab and a more sophisticated masking arrangement was assembled (Figure 4.3-1B), it was found that scatter from the mask being too far from the plate may have contributed to the problem.

It was observed that the band of emulsion around the outside of the plate caused by the drying of the rather dilute emulsion used for coating (see Figure 5.5.1) was about 3 times more sensitive than the central region of the plate.

Plates 10 and 11 show the first indication of the lack of response of the system to the dehydration step. As can be seen, this problem carried on through this series, and in fact through the entire investigation.

After plate 11, bleach and fix baths were introduced. The processing for plate 13 is as follows:

Development	10 min.	over 10% methylamine solution
Developer Wash	5 min. 5 min	20 ml. 90% methanol same
Water wash	1 min.	distilled
Fix	2 min	Kodak F-5 hardening fix
Water wash	3 min.	2.5 min. tap, 0.5 min. distilled
Beach (½ plate)	TC*	PBQ bleach
Water wash	3 min.	2.5 min. tap, 0.5 min. distilled
Fix (½ plate)	2 min.	Kodak F-5 hardening fix
Water wash	3 min.	2.5 min. tap, 0.5 min. distilled
Dehydration	3 min. 3 min.	50% isopropanol, 25°C 100% same

Dry	air at room temperature
*	to completion

Figure 5.2-1 illustrates the condition of different parts of the plate as a result of this processing.

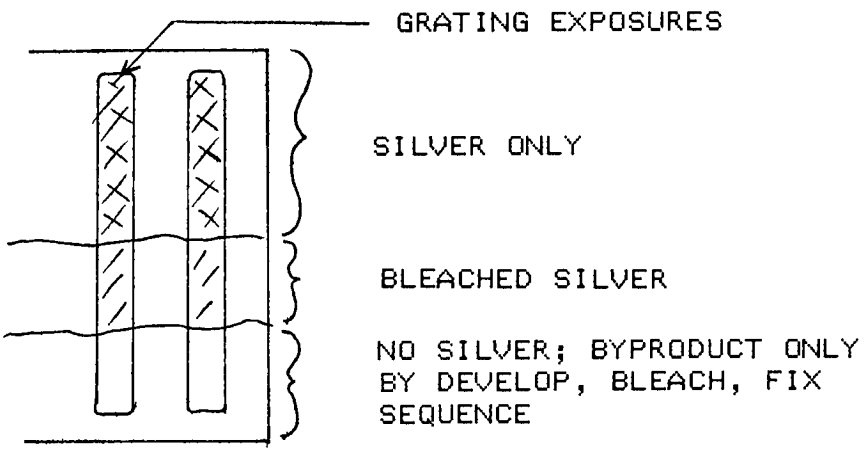


Figure 5.2-1 Plate 13 following processing.

Plate 14 was processed in a slightly different manner. The entire plate was processed. The steps are the same as above unless noted. Water wash steps are omitted:

Development	5 min.
Developer Wash	
Bleach	3 min.
Fix	
Dehydration	

This is the most economical processing sequence, step-wise, however, it gives no opportunity for measurement of any results except the final grating in gelatin with all silver

removed. With an additional drying step, the grating in gelatin before dehydration could also be measured. To obtain needed data about the behavior of the emulsion through the process, more useful processing sequences were generally employed.

Plate 15, the last plate in this series, was the most useful of the plates processed and will be described in full. Processing was as follows:

Water wash steps and processing parameters were the same as plate 13 described previously.

Development	10 min.	Significant density even at lowest exposure
Developer wash		Double wash
Bleach (3/4 of plate leaving silver strip)	6.5 min.	PBQ
Fix		F-5 hardening
Bleach (½ of remaining silver strip)	TC	Not in central portion of plate - PBQ
Dehydration		

Figure 5.2-2 shows the plate condition after this processing and Table 5.2-2 the exposure parameters and measured results.

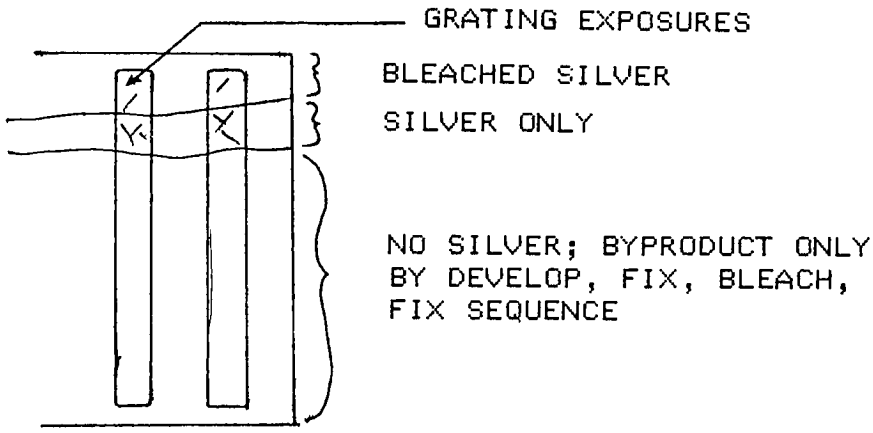


Figure 5.2-2 Plate 15 following processing.

EXP. NO.	EXP. TIME (SEC)	EXPOSURE (mJ/cm2)
1	2	1.1
2	5	2.8
3	10	5.6
4	15	8.4
5	30	16.8
6	45	25.2

	********** GRATING EFFICIENCY **********					
EXP. NO.	Ag ONLY (%)	DEHYD. Ag ONLY (%)	BLEACHED (%)	NO Ag (%)	DEHYD. NO Ag (%)	NO Ag SCATTER + ABSORPTION (%)
1	X	X	7.0	X	0	6.5
2	X	X	26.9	X	0.17	12.2
3	X	X	33.7	X	0.37	16.3
4	X	X	39.2	X	0.47	19.5
5	X	X	30.9	X	0.45	24.2
6	X	X	33.9	X	0.40	24.0

Table 5.2-2 Efficiency results for plate 15.
Developing time 10 min.
X = not measured

Plate 15 was developed to considerably higher density than previous plates. The density at exposure 1 was easily visible and that at 6 very dark. The intent of this series was not primarily to observe a dehydrated grating similar to the dichromated gel process but to substantiate the

presence of a grating resulting solely from the developer oxidation byproducts. This, indeed, was seen. There was a grating present after all silver was removed from the emulsion and the grating efficiency is seen to correlate with the bleached grating efficiency and with density, both functions of development. Also, a brownish coloration was observed, presumably the result of staining by the developer oxidation byproduct, and the density of this coloration correlated with the no silver grating efficiency. The source of the modulation of the no silver grating could be index modulation from differential hardening or dehydration, or simply amplitude modulation from the developer byproduct staining.

5.3 MINIMIZING GENERAL HARDENING

Although, at this point, a grating caused solely by the developer oxidation byproduct had been observed, a dehydrated grating similar to that characteristic of the dichromate process had not. It is known that such a grating is critically dependent on the hardening differential between the exposed and unexposed areas of the emulsion. It did not seem likely that the correct balance between these parameters could be predicted given the present meager knowlege of the behavior of the incorporated developer emulsion, and the evidence of non exposure related hardening already observed. It was decided, however, to expose a series of gratings using emulsion parameters and processing designed to eliminate as many sources of general hardening as possible.

The emulsion used in this section had the following relevant parameters:

1-11-86	Date Precipitated
10.12	Moles developer per silver mole
0.0005	Moles AgH per gram gelatin
80	% pig gelatin
20	% bone gelatin
YES	subbed plates
NIL	grams formaldehyde per gram gelatin

For these plates the incorporated developer concentration was halved again, and the gelatin hardener at coating was

eliminated. Also, the developer colloid was fresh and the plate was exposed immediately. This precaution was taken because of a reoccurring problem of oxidation of the developer colloid with storage.

The processing used was as follows:

Development	3.5 min.	Just visible density at lowest exposure
Stop bath	30 sec.	1.2% acetic acid
Developer wash		50 ml. volume of baths
NO BLEACH		(PBQ is a hardening bleach)
Fix		F-5 NO HARDENER
Dehydration		

The stop bath was added to ensure that the pH of the emulsion dropped after development and reduced the activity of the incorporated developer. Increasing the developer wash baths' volume to 50 ml. was simply to add effectiveness. The remaining changes are self evident.

The resulting gratings did not show any improvement in dehydrated grating efficiency, however, a number of interesting observations were made:

-The emulsion stood up well to processing, indicating that the formaldehyde hardening at coating was not necessary.

-After dehydration, the emulsion had a frosted appearance which disappeared if the emulsion was wetted. This is a trait which is sometimes observed in the dichromate process as a result of dehydration.

-During the fix step, a loss of density was noted in the areas of lower density.

-The fogged area around the highest exposures was much less, but still there.

The fog may have been reduced by the lower developer concentration or an improved masking arrangement (as per Figure 4.2-1B). Its presence could be explained by light scatter in the emulsion and/or tunneling of light through the glass slide.

5.4 MICROSCOPIC EXAMINATION

The failure to achieve high diffraction efficiency after dehydration led to some questions regarding the quality of the density grating obtained in the experimental emulsion. It was obvious that the grating did exist and that the quality was sufficient to obtain diffraction efficiencies from the bleached grating in the 40% range. Bleached gratings can, however, yield diffraction efficiencies in the 80% range and further evaluation of the gratings seemed appropriate.

At the input angle used, the grating was 1000 lpm. which gives a period of one micron. With a Bauch and Lomb microscope with oil immersion 100X objective and 15X ocular, the fringe structure is observable.

To provide a source of reference for observation of the test gratings, an Agfa 8E75 Holographic Plate was exposed in the same manner as the experimental plates, and developed in D19, a developer commonly used for this plate. The 8E75 plate showed a fringe structure with a very sharp differentiation between the density and non density area of the fringes. Very smooth edges along the fringes were observed.

The test gratings showed a much less smooth edge between the density and nondensity areas of the fringes. The edges were jagged and the fluctuation of the edge covered an area of about a quarter micron.

In the areas near the highest exposure on the test plates, where fog was observed to be the highest, a structure of blotches of density was observed. These blotches were on the order of a half micron in size and were observable through the volume of the emulsion.

5.5 SODIUM HYDROXIDE DEVELOPMENT

The use of a gas to raise the pH of the emulsion had a number of proposed advantages, primarily the absence of swelling of the emulsion during development. Sodium hydroxide, however, was the preferred development inducer in the original patent for this incorporated developer(92) system. Sodium hydroxide development provided a convenient quick check of emulsion developability as well as a comparison for the behavior exhibited by the emulsion under the gas development used in the experimentation.

Initial developability tests were performed with sodium hydroxide solution. It should be noted that a sodium carbonate-bicarbonate buffer solution (pH 10.0) had no effect. These qualitative tests showed that the concentration of the sodium hydroxide influenced the speed of development and the density obtained. Concentrated sodium hydroxide was found to give immediate, strong density on an exposed incorporated developer emulsion and no density on an unexposed sample. This indicated a very strong resistance of the emulsion to nonspecific development.

After the emulsion was tested with incoherent exposures and

gas development, a similar series was run with sodium hydroxide for comparison. The behavior of the emulsion (exposure and nonexposure related peeling, swelling, density developer byproduct etc.) was found to be very similar for concentrations in the tenth normal range. For very dilute sodium hydroxide solutions, however, (.001 normal range) the unexposed areas tended not to peel, while the exposed areas showed density and peeled. This pointed to better nonspecific development behavior and contributed to the conclusion that the gas development was too violent.

Also observed in this group of tests was a result which could not be later replicated but which is mentioned here because it was interesting enough to, perhaps, warrant further investigation. A small amount of sodium hydroxide solution was added to a 50 ml. volume of methanol. The emulsion, exposed with a step tablet, developed density in this solution and neither the density or nondensity areas peeled. If the emulsion was then placed in water, it peeled in both the density and nondensity areas. The solution used was estimated to be 0.006 N NaOH, 6.0% water in methanol. This was exciting because, apparently, development was taking place without swelling the emulsion. It also opened the possibility of adding sulfite to the

developing solution to control migration of developer byproduct, and thus hardening resolution.

These development conditions were replicated later in the experimental work. The emulsion used had half the amount of incorporated developer, no formaldehyde at coating, but was otherwise similar. Density was obtained with sodium hydroxide solution, but the alkali methanol gave no development. Development only resulted if the alkali methanol solution was diluted to approximately 20% water. This indicated a lack of disassociation of the sodium hydroxide in more concentrated methanol. Since these tests were run on subbed plates, the indication of swelling of the emulsion by observing peeling was lacking. This apparent discrepancy in results was not pursued or explained.

6. DISCUSSION

The fine grain emulsion produced for this project was generally successful. Precipitation was not a problem with the equipment available. The grain growth inhibitor used may have contributed to some of the developability problems encountered in the gaseous development step, however, this is not established. It is certainly questionable that such a fine grain emulsion could have been produced so easily without the inhibitor. An electron micrograph of the emulsion would have been helpful to establish the crystal structure and size of the grains, however, the demonstrated ability of the emulsion to record a 2900 line per mm. grating indicated that the crystal size was sufficiently small for the present work.

The incorporation of the 4-phenyl catechol developer proved to be very problematic. The developer could not be introduced directly into the emulsion, so it was precipitated separately and added to the emulsion before coating. This separate precipitation was refined to the point that a visually homogeneous white colloid was obtained. Close inspection showed, however, that the slurry did settle, indicating that there may have been significantly large crystals of developer present, or the

small crystals coagulated together. It was hoped that, if coagulation was taking place, the introduction of the developer slurry to the much higher gelatin content of the emulsion would disperse coagulated developer crystals.

Microscopic examination of the exposed and developed plates revealed some characteristics which could possibly be attributed to the distribution of developer in the emulsion. The grating lines were not as well defined as a commercially available holographic emulsion and fog present showed a blotched pattern of density through the emulsion.

The exact condition of the developer crystals in the emulsion is, of course, very important. Further refinement of this incorporated developer emulsion should surely include inspection of the emulsion by electron microscopy and refinement of the method of incorporation to the point where the developer crystals are uniformly dispersed and the same size or smaller than the silver halide crystals.

Another persistent problem encountered with the incorporated developer was the tendency of the developer slurry to oxidize while being stored. The immediate solution to the problem would be to always prepare the

slurry immediately before use, however, the observation of this problem casts some doubt on the keeping qualities of the coated plates. The success of the system is dependent on the careful control of the hardening differential between the exposed and unexposed areas, and a significant hardening "dark" reaction taking place in the emulsion would greatly complicate the system.

The incorporation of the developer did provide a significant advantage beyond those advantages anticipated in the design of the emulsion. The speed of the emulsion was much better with the developer incorporated. In preparing plates for microscopic examination, it was decided to expose a grating on a plate coated with the experimental emulsion minus the incorporated developer, and develop the plate in the same manner as the commercial holographic plate. This would, of course, provide a means of evaluating the effect of the incorporated developer on grating quality. An exposure of 72 $mJ/cm.^2$ still did not yield a grating with useful density while exposures on the order of 1 $mJ/cm.^2$ were required to obtain density on plates with the incorporated developer. This indicates that the incorporation of the developer could be extremely useful for the production of density gratings in a very

fine grain emulsion, even if it did not work well in the system originally proposed.

The exposure and evaluation system devised was more than adequate for the work. The only major problems were fundamental problems associated with argon lasers, that is, expense, vulnerability to failure, vibration associated with cooling the very inefficient argon laser, and scatter encountered at this short wavelength. Using this laser was, however, a reasonable trade-off for avoiding the additional complications of spectrally sensitizing the emulsion.

The development in an alkaline gas atmosphere turned out to be the single most difficult step to control and the problems introduced in this step prevented refinement of many of the originally proposed processing parameters.

In this system, development is hardening, and non specific development or fog is general hardening of the emulsion. Uncontrolled general hardening is expected to destroy the hardening differential between the exposed and unexposed area of the interference pattern recorded, and prevent successful conversion of the hardening differential to a

refractive index modulation by alcohol dehydration.

Evidence of a general hardening effect in the development step was seen when the first sample plates were developed and the emulsion peeled off the plates. The manner in which the emulsion peeled is difficult to explain. The emulsion swelled in a lateral direction by 20% to 30%. Hardening of gelatin should prevent swelling, not increase swelling. A possible explanation could be a crosslinkage along gelatin molecules which are parallel to the surface of the plate, so swelling was forced to increase the lateral dimension only. This could happen if the molecules achieved this orientation during the coating of the emulsion. Increasing the coating temperature would tend to prevent a crystaline orientation of the gelatin molecules during coating but the coating temperature used was already 50°C with a very dilute emulsion and increasing it further would cause drying problems. Another approach would be the addition of urea to the emulsion to encourage the retention of an amorphous state during drying. This was not attempted.

A second possible explanation could be the formation of a skin of hardened gelatin at the surface from the

penetration of the methylamine gas into the emulsion. This idea was discarded when the same behavior of the emulsion was observed when sodium hydroxide was used as a development inducer. The lateral swelling was easily measured, however, changes in the thickness of the emulsion were not so readily determined, and were not measured.

If the hardening action of the incorporated developer was thought to result in a change in the lateral swelling of the emulsion, such a change was not observed directly. However, the tendency of the areas of the emulsion which developed density to peel more quickly than those areas without density supported this hypothesis. Certainly the result of such a differential hardening action would be difficult to observe directly since the emulsion showed significant lateral swelling even when it was developed with no exposure.

Some explanation of the strong non exposure related hardening with the use of methylamine gas as a development inducer can be proposed. The methylamine gas used to raise the pH of the emulsion dissolves in the gelatin creating methylammonium ion and the OH^- radical. The methylammonium ion can combine with the silver halide grains to form a

soluble methylammonium complex. This combination of soluble silver salts and active developer is likely to lead to physical development, creating sufficient developer byproduct to harden the gelatin. Evidence against this proposal is the fact that visible dichroic fog was not necessarily observed along with evidence of general hardening. Perhaps the grain structure was very small. Perhaps the pig gelatin used was particularly vulnerable to hardening under these conditions.

Evidence that the methylamine gas method of inducing development was a particular problem is also illustrated by the comparison of its behavior with that of sodium hydroxide as a development inducer. At NaOH concentrations of tenth normal, the behavior of the emulsion was very similar to that of methylamine gas. At much lower concentrations, however, density was obtained (with peeling) and the unexposed, non density areas did not peel. This indicated a much better hardening differential between the exposed and non exposed areas or, stated differently, a much lower general hardening of the emulsion under conditions which produced density.

Subsequent use of the gas development method revealed

additional problems with reproducibility. The concentration of the vapor in the developing chamber was critical and was influenced by stirring and temperature. Even when a reasonably stable developing chamber had been devised, reproducibility continued to be a problem and other factors were suspected. Migration of the gas into the emulsion was considered. With the method of coating used, a band of emulsion around the edge of the plate could be observed which had a different appearance than the center of the plate. The difference was assumed to be thickness and the outside band was assumed to be thinner than the remainder of the plate, however, this was not measured. It was noted that when used for gas development, the outside band of the plates required about a third the exposure of the inside area to obtain the same density. The migration of the methylamine gas into the emulsion was a possible explanation, and the reproducibility of the development procedure was thought to be influenced by the permeability of the individual plates to the methylamine gas.

The subbing of the plates eliminated the peeling problem and modifications were made to try to reduce general hardening in the development step. Processing changes to

more effectively remove the developer from the emulsion following development were also introduced. The additional processing steps necessary to enable the evaluation of the alcohol dehydration step were added. No response to alcohol dehydration was observed. Given the problems already encountered with gas development, further refinement of post development processing steps to effect response to alcohol dehydration seemed futile.

It was possible, however, to link the hardening action of the developer byproduct to holographic grating formation. The assumption had to be made, however, that gelatin hardening and developer byproduct staining were the same. The original parameters of minimal development and silver grain growth intended to enhance the performance of a dichromate like recording material were discarded, and a grating with high density was exposed and developed(plate 15). With all silver removed, a grating was observed. It was not determined if the grating modulation was the result of a weak refractive index modulation from hardening action of the developer or an amplitude modulation from the stain, or both.

Failure of the dehydration step could probably be

attributed to hardening differential problems, and there were still several easily eliminated sources of hardening in the process used. It was decided to eliminate these sources of hardening as a last attempt for an easy solution to the lack of response to dehydration. The resulting grating did not respond to dehydration. However, the emulsion did develop a "frosted" appearance from the dehydration step which disappeared if the emulsion was moistened. This was considered encouraging since this frosted appearance is commonly observed in the dichromate process. It was not considered encouraging enough, however, to continue pursuing the dehydration step with so many recognized problems with previous steps in the process.

7. CONCLUSION

The body of work performed for this project resulted in an indication of the feasibility of the proposed incorporated developer, dichromate like holographic recording system and the problems associated with such a system.

Some aspects of the system showed considerable promise for use in the proposed holographic recording system. The fine grain emulsion was successfully precipitated and the incorporation of the developer produced considerable advantages in emulsion speed over more conventional development techniques. The incorporation of the developer posed some problems with crystal size and keeping qualities but nothing that would appear insolvable.

However, the system, as proposed, did not look very promising, primarily because of the problems encountered with the methylamine gas developing step. General hardening of the gelatin and irreproducibility were the most important problems. These problems were very serious and no potential solutions were discovered.

Development methods other than gas development could possibly be used with the intention of producing a

dichromate like result. Sodium hydroxide showed considerably more promise as a development inducer than the gas development but was not investigated in depth. Although sodium hydroxide solution development would give up the proposed advantage of not swelling the emulsion during development, this is not known to be a necessary prerequisite, and useful developer byproduct image-wise hardening could result.

There was some experimental evidence that the emulsion could be raised in pH without swelling by an organic alkali solution. The experimental results were very inconclusive, but the approach is worth some thought. If the emulsion could extract the alkali radical from an organic without appreciable absorption of water, the pH change could be effected without swelling.

From the perspective of a more conventional holographic recording material, that is, an emulsion intended to produce a silver image which is subsequently bleached, the material has some interesting possibilities. A very fine grain emulsion with good speed is very appealing for holography and for silver halide imaging in general. If the methylamine gas development indeed limits swelling of

the emulsion perpendicular to the plate, this could be an advantage for holographic recording since it would minimize distortion of the fringe pattern from changes in emulsion thickness.

APPENDIX A - PROCESSING SOLUTION RECIPES

Kodak D19 developer:

Metol	2.0 grams
Sodium Sulphite (anhydrous)	75.0 grams
Hydroquinone	9.0 grams
Sodium Carbonate (monohydrate)	30.0 grams
Potassium Bromide	5.0 grams
Water to make	1.0 liter

Kodak F-24 non-hardening fixer:

Sodium Thiosulfate (Pentahydrate)	240.0 grams
Sodium Sulfite (Anhydrous)	10.0 grams
Sodium Bisulfite (Anhydrous)	25.0 grams
Water to make	1.0 liter

Kodak F-5 hardening fixer

Sodium Thiosulfate (Pentahydrate)	240.0 grams
Sodium Sulfite (Anhydrous)	15.0 grams
28% Acetic Acid	48.0 milliliters
Boric Acid Crystals	7.5 grams
Potassium Alum, Fine Granular (Dodecahydrated)	15.0 grams
Water to make	1.0 liter

APPENDIX B - SUBBING METHOD

Subbing solution:

Bone gelatin	5.0 grams
Chromium alum	0.5 grams
Water to make	1.0 liter

1. Clean glass in chromic acid.
2. Wash in distilled water.
3. Leave in water until ready for subbing.
4. Immerse plate in subbing solution at a 45 degree angle.

   Withdraw at 45 degrees and dry.

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